Today nano scale materials are being used for wide range of applications. One promising topic in nano scale materials is using them for reinforcement of different polymeric materials to reach desirable stiffness properties. The stiffness of these materials is mostly found experimentally because the nanocomposite community lacks decent analytical model that can provide reliable prediction. Modeling can be done using both numerical and analytical methods. Numerical methods can be time consuming, expensive and need expertise to implement right assumptions and extrapolate useful data. But they can be more reliable, if done correctly, compared with the analytical method. Analytical methods use a mathematical equation that has been derived considering the physics of the problem. Analytical methods are equations that predict properties on nanocomposites based on properties of components at different conditions (e.g., temperature, and more) and are more desired. For this work we used a new Monte Carlo finite element analysis (FEA) method as a numerical method to model the stiffness of different nanocomposites and compared them with different analytical models to find the most accurate model that can predict the stiffness of nanocomposites as a function of its components? properties. We then compared different models with experimental results using cellulose nanocrystal composites.
Developing Design Model for Cellulose Nanocomposites

by

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

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Meisam Shir Mohammadi, Author
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DEDICATION

I dedicate this dissertation to my family especially my parents for being always supportive. They always put our dreams (my brother and I) their priority, and encourage me to take risk and never be afraid of failure.
Study hard what interest you the most, in the most undisciplined, irreverent and original manner possible.

Richard Feynman

1

Introduction

The primary goal of this project was to develop a design model that can predict the mechanical properties of nanocomposites. By definition, a particle is considered nano material if the particle’s size, in at least one dimension, is between 10 - 1000 nm. The concept is attractive due to possibility for development of nanocomposites with unique mechanical, electrical, thermal and optical properties. These properties are achievable using nanoparticles because of their high surface area per volume, and lower defects compared with larger particles. However, using nanoparticles has some drawbacks. Most nanoparticles are expensive and hard to fabricate. Due to high surface area they tend
to agglomerate (poor dispersion) in composites and it is hard to measure properties of nanocomposites. So fabrication of nanoparticles are challenging. Developing models that could predict the property of nanocomposites can be useful in two ways. First, before fabrication, which makes it possible to predict the properties of nanocomposites in different conditions and check if desired properties can be reached or not. Second, is for validating the experimental results and check how far it is from the ideal condition.

Here we focus on mechanical properties of nanocomposites specifically the stiffness modulus. The nanocomposite community lacks a decent model that predict the stiffness of nanocomposites because most of traditional models have poor outcome on predicting properties of nanocomposites. Modeling can be done using both numerical and analytical methods. In numerical methods (or computer modeling) we divide a big problem into small problems (based on continuum mechanics) and solve them independently and have the overall results. General numerical method for mechanical properties of composite is finite element analysis (FEA). FEA method in traditional composites accurately predict modulus of composite but for nanocomposites sometimes underestimates the properties which will discuss the problem, and the solution. In the second chapter we use a new Monte Carlo FEA with bounded displacement boundary condition (BVE) to numerically model the stiffness properties of different nanocomposites, compare the results with the most accepted analytical model for stiffness prediction of composites in micro mechanic and introduce a new model which, in our believe, is more accurate for prediction of stiffness in composites. In the other word, in first chapter we show why the traditional composites models (both numerical and analytical) cannot be reliable for nanocomposites.

Generally, numerical methods are time consuming, expensive and need expertise to implement the right assumptions and extrapolate useful data. Also they can be reliable if they are done correctly. But, analytical methods are more preferably if they are available. Basically analytical model is a mathematical equation that has been derived by
considering the physics of the problem. So, analytical methods can predict properties on nanocomposites based on properties of its components at different conditions (e.g., temperature, moisture and more) and are more desired compare with numerical methods. Here, in the third chapter, we use Monte Carlo FEA results as a numerical method to model the stiffness of different nanocomposites and compare with analytical models to find most accurate model that can predict the stiffness of nanocomposites as a function of its components’ properties. Moreover, In the fourth chapter, we evaluate all analytical models that are being used - in our knowledge, for stiffness prediction of nanocomposites and compare them with experimental results of cellulose nanocrystal (CNC) composites, and expand the comparison to other nanocomposites.

The reason for choosing cellulose nanocrystals (CNC) for our experiments is that CNCs are inexpensive renewable nanoparticles that can be extracted from different sources (wood, cotton, tunicate, bacteria and more). CNC can be extracted with two major methods - Mechanical or chemical extraction. Briefly, in mechanical methods, cellulose is broke down to nano scale using mechanical shear and it is usually called cellulose nanofiber (CNF). In chemical process (using acid hydrolysis or liquid ion) amorphous parts of cellulose are dissolved and only crystalline parts are left (CNC). The crystal structure, size of nanofibers, surface property of nanocrystal, their stiffness and other properties vary depending upon the source and extraction process. Cellulose nanocrustals have high stiffness (it is comparable with steel, nanoclay and carbon nanotubes). CNC has been used to reinforce different polymers from soft rubbery to high stiffness glassy. So using CNC nanocomposites we had wide variety of nanocomposites to compare with the analytical models.

After this comprehensive study on the stiffness of nanocomposites, in the fifth chapter we introduce a method for fracture toughness measurement of nanocomposites which in our believe is being misunderstood in nanocomposite community (rubbery nanocompsites
in particular). And in the sixth chapter we introduce a method for fabrication of flexible sensors with tunable properties using cellulose nanocrystals.
2

Numerical and Analytical Modeling of Aligned Short Fiber Composites including Imperfect Interfaces

Finite element calculations were used to bound the modulus of aligned, short-fiber composites with randomly arranged fibers, including high fiber to matrix modulus ratios and high fiber aspect ratios. The bounds were narrow for low modulus ratio, but far apart for high ratio. These numerical experiments were used to evaluate prior numerical and
analytical methods for modeling short-fiber composites. Prior numerical methods based on periodic boundary conditions were revealed as acceptable for low modulus ratio, but degenerate to lower bound modulus at high ratio. Numerical experiments were also compared to an Eshelby analysis and to an new, enhanced shear lag model. Both models could predict modulus for low modulus ratio, but also degenerated to lower bound modulus at high ratio. The new shear lag model accounts for stress transfer on fiber ends and includes imperfect interface effects; it was confirmed as accurate by comparison to finite element calculations.

2.1 Introduction

In mean-field modeling of short-fiber composite materials, a composite unit cell is subjected to mean stress or strain and the effective stiffness or compliance tensors are found by averaging strains and stresses throughout the composite \[1\]. This averaging is done over all unit cell orientations using a fiber orientation distribution function. The unit cell for this analysis is a short fiber composite with all fibers aligned in the same direction. Thus, the fundamental problem for analysis of short-fiber composites is to determine mechanical properties of an aligned, short-fiber composite.

One might think this problem is solved by methods such as Eshelby \[2\], Mori-Tanaka \[3\], modern shear-lag models \[4, 5, 6, 7\], or numerical methods \[8, 9, 10, 11, 12, 13\], but some gaps appear. First, most prior numerical studies have been limited to modest fiber/matrix modulus ratios of \( R = E_f/E_m < 30 \) and relatively short fiber aspect ratios, \( \rho = l_f/d_f < 30 \) \[8, 9, 11, 13\]. Gusev and Lusti \[10, 12\] looked at higher aspect ratios, but only for a narrow selection of \( R \) and fiber volume fraction, \( V_f \). As a consequence, the validation of analytical models by these numerical studies \[9\] only validates them for the corresponding small range of properties.
A recent trend in composites research, especially in nanocomposites, is to reinforce soft polymers (e.g., elastomers with $R > 10^4$) and isolate nano-fibers with aspect ratios higher than 30 [14, 15, 16, 17]; the results of such work has been a challenge to model. Figure 2.1.0.1 shows some experimental results for reinforcement of an elastomer with nano-cellulose fibers [14] and compares them to an existing analytical model (labeled “Mori-Tanaka” [3]) and an existing numerical method based on large periodic representative volume elements (RVEs) with randomly placed fibers (labeled “Periodic RVE (FEA)” using approach of Gusev [8]). These experimental results are two to three orders of magnitude higher than existing models. The question arises — are these high reinforcements the discovery of a new nano-phenomenon that cannot be modeled with continuum mechanics or do continuum methods just need to be revised for high $R$? To explore this question, we developed a new numerical method to derive upper and lower bounds to the modulus. The sample calculation of bounds in Fig. 2.1.0.1 (see dashed lines) shows that experimental results fall within continuum mechanics bounds and that prior modeling methods all degenerate to lower bound results. In other words, the methods described here have new potential to guide expectations of properties for composites with high $R$.

To study composite modeling methods at high $R$ and aspect ratio as well as how they relate to conventional methods at low $R$ and aspect ratio, we ran numerical calculations for a very wide range of $R$ (from 10 to $10^5$) and aspect ratios (from 5 to 100). The calculations in this part of the study were based on novel methods that allowed us to numerically determine upper and lower bounds to the fiber-direction modulus. The shear number of calculations along with the size of mesh (particularly at high aspect ratio) precluded mesh refinement of numerical results. A powerful feature of the bounding method, however, is that it allows one to get definitive bounds even without mesh convergence. These numerical results provided input for considering four questions:
Figure 2.1.0.1: The symbols are experimental results from Ref. [14] with $R = 9.5 \times 10^5$, which are compared to existing modeling methods (Mori-Tanaka and Periodic RVE (FEA)) and to upper and lower bounds described in this paper (dashed lines). The experiments are quasi-2D with fibers claimed to be randomly aligned in the plane of a film. The models are 2D calculations for aligned fibers. The comparison with experiments is only qualitative, but if experiments had aligned fibers, they would move toward the upper bound and still demonstrate that prior models are near the lower bound and far below experiments.

What is correct modulus? One of the best ways to judge the accuracy of modeling methods is to compare them to numerical results [9], but what numerical method gives the correct modulus? Here we derived numerical bounds using Monte Carlo methods with randomly placed and well-dispersed, aligned fibers. We used bounding methods to define limits on the modulus for $R$ up to $10^5$ and $\rho$ up to 100. The separation of the bounds shows that the calculated modulus depends on boundary conditions, especially for large $R$.

How do periodic RVE calculations compare to numerical bounds? Most numerical models use periodic RVEs and assume analysis results with periodic boundary conditions are equivalent to bulk composite properties. To test this hypothesis, we compared the new numerical bounds to both small periodic RVEs (using either cylindrical (rectangles in 2D) or elliptical fibers) and large RVEs with random fibers. All periodic RVE methods work well for low $R$, but degenerate to lower bound results at high $R$. 
Can an analytical model sufficiently capture the results of periodic RVE composites?

Given the capabilities (and limitations) of periodic RVE analysis, an analytical model that agrees with those numerical results would have those same capabilities (and limitations). We developed an improved shear-lag model for short fiber composites that explicitly includes stress transfer on the fiber ends and imperfect interfaces. The new model, along with an Eshelby [2] analysis, were compared to numerical results on the same geometries. These analytical methods can reproduce numerical methods based on periodic conditions, which means they give good prediction for low $R$, but degenerate to lower bound results for high $R$.

Can an analytical model account for 3D fibers and for imperfect interfaces? The first three questions used 2D calculations and assumed perfect fiber/matrix interfaces. Real composites are 3D and may have imperfect interfaces. We lastly considered 3D single fiber RVE results by comparing axisymmetric numerical calculations with imperfect interfaces to the new shear lag analysis with concentric cylinders that also includes imperfect interface effects. The new model accurately reproduces all numerical results including the role of imperfect interfaces.

2.2 Methods

All finite element calculations (FEA) were linear elastic, static, and two dimensional. Most simulations were plain strain analyses although some 3D results were generated using axisymmetric simulations. All calculations were done using the open source code NairnFEA [18] with 8-node quadrilateral elements. Issues involving convergence are discussed in section 2.3. By using script control, we automated the thousands of FEA calculations needed to get sufficient results for answering the posed questions. The FEA calculations were run on either desktop computers or Linux nodes in a cluster. The main
requirement for the largest calculations was to have sufficient memory (more than 5 GB).

2.3 Results and Discussion

2.3.1 What is the Correct Modulus?

To run numerical experiments for the “correct” modulus of aligned short fiber composites, we ran FEA calculations on representative composites with randomly placed fibers. The fibers were all aligned in one direction, placed using a random sequential adsorption (RSA) method [11], and well dispersed (separated by at least one element in the mesh). The numerical experiments were done for fiber to matrix modulus ratios of $R = 10, 100, 1000, 10^4, \text{ and } 10^5$, for fiber aspect ratios of $\rho = 5, 10, 20, 40, 70, \text{ and } 100$, and for fiber volume fractions of $V_f = 0.01, 0.02, 0.05, 0.1, 0.15, 0.2, \text{ and } 0.25$. Monte Carlo methods were used to account for the random structures. For each combination of $R, \rho, \text{ and } V_f$, we ran FEA calculations for 20 random structures and averaged the results for mean and standard deviation of the modulus. For most property settings, the 20 replicates gave sufficiently narrow errors bars on the results. The total number of FEA calculations required to map the parameter space exceeded 15,000.

The first issue was the mesh. To deal with randomly placed fibers with randomly situated stress concentrations, the modeling used a regular mesh. A quick calculation showed that a 3D mesh for the largest aspect ratio would have over a billion degrees of freedom, which is infeasible for the 15,000 calculations we needed to run. 3D calculations by Gusev [8] required 30 processor-hours per calculation and that was for spherical inclusions ($\rho = 1$) which can use much smaller RVEs then needed here. We therefore switched to 2D, plain-strain FEA (which still can be used to evaluate other methods provided comparisons are made to 2D versions of those methods). Even in 2D, the mesh could not
be highly refined. We used the crudest mesh possible where the element size was equal
to the fiber diameter. Thus each fiber had one element across its width and the well-
dispersed fibers were separated by at least one fiber diameter \( (i.e., \text{one mesh element}) \). With this mesh, the largest calculation had about 200,000 degrees of freedom and could be completed in a 5-30 minutes (depending on computer speed).

Because we were limited to a crude mesh, we could not refine the mesh for convergence. To allow definitive results with such a mesh, we adopted a bounding method. In composite variational mechanics, upper and lower bound results are found by solving the two problems in Fig. 2.3.1.1 [1, 19, 20, 21]. First, the composite is subjected to constant tractions, \( T \), over the entire surface of

\[
T = \sigma_0 \cdot \hat{n}
\]

where \( \sigma \) is the uniform applied stress and \( \hat{n} \) is surface normal. For stress corresponding to axial loading in the fiber direction (see Fig. 2.3.1.1A), the complementary energy, as approximated by FEA strain energy \( (\Gamma_{FEA}) \), must be greater than or equal to the exact complementary energy, \( \Gamma \), leading to

\[
\Gamma_{FEA} \geq \Gamma = \frac{\sigma_0^2 V}{2E_{yy}^{(r)}} \quad \text{or} \quad E_{yy}^{(r)} \geq \frac{\sigma_0^2 V}{2\Gamma_{FEA}} = E_{LB}
\]

where \( V \) is specimen volume and \( E_{yy}^{(r)} \) is the effective, plain strain modulus in the \( y \) direction. In other words, an FEA calculation of \( \Gamma_{FEA} \) provides a lower bound to the axial modulus \( (E_{LB}) \).

Second, the composite is subjected to a uniform strain field, which corresponds to fixed displacement (in both directions), \( u \), over the entire surface of

\[
u = \varepsilon_0 \cdot x
\]
where $\varepsilon_0$ is the applied strain and $x$ is position on the surface. For such fixed-strain conditions (see Fig. 2.3.1.1B), the FEA strain energy ($U_{FEA}$) is a rigorous upper bound to the exact strain energy, $U$, leading to

$$U_{FEA} \geq U = \frac{1}{2} \varepsilon_0 \cdot C \varepsilon_0 V \quad (2.3.4)$$

where $C$ is the effective stiffness tensor. Numerical calculation of axial modulus when using fixed-strain boundary conditions requires three separate FEA calculations:

1. Use $\varepsilon_x = \varepsilon_0$, $\varepsilon_y = 0$, and $\gamma_{xy} = 0$. An FEA calculation gives $C_{11} \leq 2U_{11}/(\varepsilon_0^2 V)$ (where $U_{11}$ is the strain energy from that FEA analysis).

2. Use $\varepsilon_x = 0$, $\varepsilon_y = \varepsilon_0$, and $\gamma_{xy} = 0$. An FEA calculation gives $C_{22} \leq 2U_{22}/(\varepsilon_0^2 V)$.

3. Use $\varepsilon_x = \varepsilon_0$, $\varepsilon_y = \varepsilon_0$, and $\gamma_{xy} = 0$. An FEA calculation gives $C_{11} + C_{22} + 2C_{12} \leq$
A reduced plain-strain axial modulus can be found from these three results using

$$E_{yy}^{(r)} \leq \frac{2}{\varepsilon_0^2 V} \left[ U_{22} - \frac{(U_{12} - U_{11} - U_{22})^2}{4U_{11}} \right] = E_{UB}$$ \hspace{1cm} (2.3.5)

The plain strain properties are defined from the reduced compliance tensor, $S^{(r)}$, which is the inverse of the stiffness tensor found by 2D FEA:

$$\begin{bmatrix}
C_{11} & C_{12} & 0 \\
C_{12} & C_{22} & 0 \\
0 & 0 & C_{66}
\end{bmatrix}^{-1} = S^{(r)} = \begin{bmatrix}
1/E_{xx}^{(r)} & -\nu_{xy}^{(r)}/E_{xx}^{(r)} & 0 \\
-\nu_{xy}/E_{xx}^{(r)} & 1/E_{yy}^{(r)} & 0 \\
0 & 0 & 1/G_{xy}^{(r)}
\end{bmatrix}$$ \hspace{1cm} (2.3.6)

A side benefit of the three upper bound calculations is that they can also determine $E_{xx}^{(r)}$ and $\nu_{xy}^{(r)}$. One more calculation with $\varepsilon_x = \varepsilon_y = 0$, and $\gamma_{xy} = \gamma_0$ can add the fourth (and final) in-plane property, $G_{xy}^{(r)}$. The results here focus on $E_{yy}^{(r)}$ although some comments on other properties are at the end.

Formally, neither the lower bound in Eq. (2.3.2) nor the upper bound in Eq. (2.3.5) are rigorous bounds. A rigorous lower bound requires complementary energy. Here we assumed strain energy found under stress boundary conditions is a good approximation to complementary energy. Although fixed-strain conditions give rigorous upper bounds to the elements of $C$, Eq. (2.3.5) combines those bounds to find a modulus that may not be a rigorous upper bound to axial modulus. Because the second term in Eq. (2.3.5) is generally small ($\leq 2\%$ of $U_{22}$, especially at higher $R$ and $V_f$), $E_{yy}^{(r)}$ is effectively a rigorous
upper bound property. We therefore took these two results as defining bounds for the composite modulus.

The next issue was the size required for the bounded volume element (BVE). It should be large enough that results are unaffected by its size, but small enough to keep calculation times reasonable. Figure 2.3.1.2A plots $E_{yy}(LB)$ for fixed traction (solid curves) and upper bound $C_{11}$ for fixed strain (dashed curves) as a function of the length of the BVE relative to the fiber length ($L/L_f$) for fixed width of 20 times the fiber diameter ($d_f$). These results are for fiber volume fraction $V_f = 10\%$, modulus ratio $R = 10^5$ (more details on fiber properties are given below), and two fiber aspect ratios ($\rho = 10$ and 100); they include the extreme cases with the largest value of $R = 10^5$ and largest $\rho = 100$. Figure 2.3.1.2B shows analogous results as function of width of the BVE relative to fiber diameter ($W/d_f$) for fixed length of $10L_f$ and a different $R = 10^2$. For BVE with short $L$, it is likely for fibers to span the entire length of the BVE resulting in an artificially high modulus that approaches the continuous fiber composite. As $L$ increased, the modulus decreased and plateaued above $L/L_f$ in the range of 5 to 10. Similarly, the magnitude of the error bars
decreased up to about $L/L_f = 10$. All subsequent simulations used $L/L_f = 10$. For short width BVE, the modulus bounds were widely separated, but moved closer as $W$ increased. They plateaued at about $W/d_f = 40$. Width effects at higher $R = 10^5$ showed a small amount of continued decrease in the upper bound result for $W/d_f > 40$. The decrease, however, was relatively small. Because using larger $W$ made simulations impractical, all subsequent simulations used $W/d_f = 40$. Note that this BVE size is larger than some published RVE results. For example, Gusev and Lusti [10, 12] used $L/L_f \sim 3$ and $W/d_f \sim 12$. We expect that the nature of fixed strain boundary conditions, as opposed to periodic boundary conditions used in other FEA methods, is the cause of the need for BVEs to be larger than other RVEs.

**Remark 1:** Traditional RVE methods (e.g., [10, 11, 12, 13]) use periodic boundary conditions where displacements normal to an edge are constant (such that plane sections remain plane) while tangential displacements are a degree of freedom [9]. These prior boundary conditions are neither fixed strain nor fixed traction. While they may converge to a result, they provide no information on where they fall relative to upper and lower bounds (i.e., how those boundary conditions affect the converged result). The boundary conditions used here to get bounds are different. The sample calculations in Fig. 2.1.0.1 suggest that traditional methods degenerate to lower bound results, while the bounding method has the potential to bracket experimental results. To distinguish the fixed strain or traction boundary conditions used here from traditional RVE methods, the new method is labeled as a BVE method for bounded volume element.

**Remark 2:** Although a BVE model can formally describe a periodic structure, it seems unrealistic to assume fixed strain on the edge of a full-scale composite would translate to fixed strains on representative subelements of the composite. Instead, the BVE method is best imagined as external boundary conditions on a full-scale composite (albeit, a small one). When imagining a full-scale composite, it could be inconsistent to
require the BVE to be geometrically periodic (as commonly done for RVEs in traditional methods \cite{10}). Nevertheless, we compared geometrically non-periodic BVE calculations to some periodic ones and the differences were negligible for the size BVEs used.

Using the above method and BVE size, we ran all combinations of $R$, $\rho$, and $V_f$; some selected results are discussed here (other results are in subsequent sections). All simulations used an isotropic, elastic, high-modulus fiber with reduced plain strain modulus $E_f^{(r)} = 100,000$ MPa and Poisson’s ratio $\nu_f^{(r)} = 0.33$ (the unreduced properties were $E_f = 93,843$ MPa and $\nu_f = 0.2481$). The plane strain matrix modulus varied as $E_m = E_f/R$ and its Poisson’s ratio was the same as the fiber’s. Figure 2.3.1.3A shows axial modulus for $R = 100$ for three selected aspect ratios. The dashed curves are the lower bound and the solid curves are the upper bound. As expected, the modulus increased as volume fraction increased, but the increase is non-linear. The initial slope is low indicating low volume fraction does a relatively poor job of providing modulus. The slope gradually increased indicating increased fiber effectiveness at higher volume fraction. The error bars are rather small — in most cases smaller than the size of symbols used in the plots. Figure 2.3.1.3B shows the same results for $R = 10^5$ (on a log scale). Unlike the $R = 100$ results, these results have lower bound modulus that is three orders of magnitude below the upper bound. Furthermore, the upper bound results have higher error bars; the coefficient of variation was over 100% at low $V_f$, but decreased to a range of 40% to 20% for $V_f$ from 0.15 to 0.25.

Differences between upper and lower bounds in analytical modeling are well known to increase as $R$ gets larger \cite{11}. But those differences are attributed to approximations in the modeling while numerical results are commonly assumed to hone in on the correct answer and therefore upper and lower bounds should be the same. The question remains — are the differences between upper and lower bounds because the FEA is not converged or something else? To answer this question, we refined the mesh. We could most refine
Figure 2.3.1.3: Axial composite modulus for $R = 100$ (A) and $R = 10^5$ (B) for three aspect ratios as a function of fiber volume fraction. The symbols are Monte Carlo BVE results with error bars indicating their standard deviations. The dashed and solid curves connecting the symbols indicate lower and upper bounds, respectively. Note that (A) uses a linear scale while (B) uses a log scale to better visualize all results.

the mesh for the shortest fiber with $\rho = 5$. Figure 2.3.1.4 gives modulus as a function of mesh element size for $R = 100$ and for $R = 10^5$ when $\rho = 5$ and $V_f = 0.25$. As the mesh was refined, the upper bound dropped, while the lower bound was nearly constant. We estimated converged results by extrapolating to zero element size and a discrepancy that was outside errors bars (as calculated by least squares fits with error estimations) remained between upper and lower bound results. In other words, part (probably most) of the difference between stress and strain boundary conditions is that even exact solutions for upper and lower bounds differ. This observation is an effect of the heterogenous BVE. For homogeneous materials, the two boundary conditions used here would give exactly the same results; for heterogeneous materials, however, the effective modulus depends on the boundary conditions. As a consequence, one cannot define the “correct” composite modulus without specifying the boundary conditions as well. The challenge is to determine which results most accurately describe the full-scale composite. This boundary condition effect is a function of $R$. For $R < 100$, which comprises the range of most conventional composites, the boundary condition effect is relatively small ($\leq 20\%$).
Figure 2.3.1.4: Axial composite modulus for $\rho = 5$ and $V_f = 0.25$ and $R = 100$ (A) or $R = 10^5$ (B) as a function of element size. The lines extrapolate to zero element size or a mesh with an infinite number of elements. The symbols are Monte Carlo BVE results with error bars indicating their standard deviations.

But for high $R$, the effect becomes very large (1 to 3 orders of magnitude).

Lastly, we emphasize the BVE bounds are just that — bounds to axial modulus — and should not be construed as a “solution” for modeling composites with high $R$. Indeed, Fig. 2.3.1.4 shows that the upper bound decreases (by a factor of 2) for a refined mesh when $\rho = 5$ (we do not know how much it would decrease for large $\rho$). Similarly, Fig. 2.3.1.2 shows the upper bound might decrease further if the BVE was made much wider. Nevertheless, the bounds presented here remain as valid bounds to composite properties, even if they are not the best bounds that could ever be obtained. If experimental results are discovered that exceed these upper bounds, those results potentially indicate a new reinforcement mechanism that needs further study. On the other hand, any experiments bracketed by these bounds may be conventional reinforcement that can be explained by continuum mechanics.
2.3.2 How do periodic RVE calculations compare to numerical bounds?

Most numerical models analyze composite unit cells containing from one or two fibers \[9\] to many fibers \[8\]. Figures 2.3.2.1A and B show the two simplest, 2D, periodic structures with parallel or staggered fibers and with dashed lines indicating the smallest repeating unit cells. The parallel structure can be modeled with a single fiber unit cell while the staggered structure requires a unit cell with two complete fibers (each of these can model one quadrant of the unit cell by symmetry). Figure 2.3.2.1C shows a geometrically periodic structure with many fibers subjected to periodic displacement boundary conditions. Models that use any of the unit cells in Figure 2.3.2.1 assume the results reflect the full composite. This section compares results from these periodic structures to the numerical bounds from BVE experiments.

Figure 2.3.2.2 shows the meshes used to model the parallel structure with either rectangular or elliptical fibers (elliptical fiber models were done for comparison to elliptical-fiber-based Eshelby \[2\] method in the next section). An unknown parameter for an encapsulated fiber is how much matrix is above the fiber and how much is on the sides? We choose this parameter by setting the distance from the fiber end to the top of the mesh,
\( \Delta \), to equal the distance from the side of the fiber to the edge of the mesh. Under this assumption, the rectangular fiber volume fraction is:

\[
V_f = \frac{r_f L_f t}{r_m L_m t} = \frac{\rho r_f^2}{(r_f + \Delta)(\rho r_f + \Delta)} \tag{2.3.7}
\]

where \( t \) is the 2D thickness. This quadratic equation is easily solved to find \( \Delta \) for input modeling parameters \( \rho, r_f, \) and \( V_f \). For comparing rectangular to elliptical fibers, we kept aspect ratio \( \rho = L_f/(2r_f) = a/b \) and fiber area (which is also \( V_f \) in 2D) constant resulting in

\[
2L_f r_f = 4\rho r_f^2 = \pi \rho b^2 = \pi ab \tag{2.3.8}
\]

or

\[
b = \frac{2r_f}{\sqrt{\pi}} \quad \text{and} \quad a = \frac{2\rho r_f}{\sqrt{\pi}} \tag{2.3.9}
\]

where \( a \) and \( b \) are the major and minor axes of the ellipse. The distance from the top and side of the ellipse to the edge is now found by solving the quadratic equation for \( \Delta \) defined from

\[
V_f = \frac{\pi ab t}{2r_m L_m t} = \frac{\pi \rho b^2}{4(b + \Delta)(\rho b + \Delta)} \tag{2.3.10}
\]

The meshes for the two fiber unit cells (i.e., staggered structure) were similar, but considered only rectangular fibers. The meshes for the many-fiber periodic structure were regular grids with one element across the fiber width (i.e., same as in BVE calculations) and rectangular fibers only. We did periodic FEA calculations for selected combinations of \( R, \rho, \) and \( V_f \) used in the BVE modeling. Unlike the BVE modeling, we were able to refine the one- and two-fiber unit cell meshes and reach convergence by subdividing the elements in Fig. 2.3.2.2 until results became constant (the converged meshes had six elements across the fiber diameter).

First, we analyzed each periodic structure using periodic boundary conditions (e.g.,
Figure 2.3.2.2: The finite element meshes along with definition of geometric parameters for single-fiber, unit cell models for the parallel structure with either rectangular or elliptical fibers. For clarity, the boundary conditions were omitted and the mesh is shown coarser than the actual mesh used for converged calculations.

We considered two causes for periodic FEA being lower bound results and far from upper bound results for high $R$. First, the parallel and staggered unit cells were converged
Figure 2.3.2.3: Axial composite modulus for $\rho = 20$ as a function of fiber volume fraction for $R$ from 10 to $10^5$. A. Compares results of periodic unit cells to BVE bounds. B. Compares fixed traction analysis of the parallel structure to lower bound BVE results. The dashed and solid curves are elliptical and rectangular fibers, respectively. The dashed-dotted lines in A are for numerical analysis of a staggered structure. The filled triangular symbols (with error bars) in A are for Monte Carlo analysis of many-fiber unit cells with periodic boundary conditions. The open symbols (with error bars) are upper bound (squares) and lower bound (circles) BVE results.

results while the BVE results bounds were non-converged results. But, this difference cannot explain the observations, because upper bound BVE results do no converge to lower bound results with a more refined mesh. For example the results in Fig. 2.3.1.4B show that BVE results for $R = 10^5$ and $\rho = 5$ for $V_f = 0.25$ extrapolated to zero element size give upper and lower bound moduli of $492 \pm 202$ MPa and $2.15 \pm 0.05$ MPa, respectively. In contrast, the results for parallel structure with periodic boundary conditions gave $E_{yy}^{(r)} = 2.9$ MPa, which is two orders of magnitude below the upper bound and very close to the lower bound.

Second, we considered the boundary conditions. An alternate approach to periodic boundary conditions is to apply the fixed-strain boundary conditions used for the BVE. This effect clearly can explain the differences. When fixed-strain boundary conditions are applied to the many-fiber unit cell, it is converted essentially into the BVE method and matches the upper bound results. The only difference is the geometrically periodic
structure, which as mentioned above has negligible affect on BVE results. The fixed-strain method, however, does not work well for parallel and staggered structures because the final result depends on the choice of unit cell (e.g., quadrants of unit cells 1 or 2 in Fig. 2.3.2.1A and B). This dependence is caused by variable amount of fiber material contacting the fixed-strain boundary conditions. In other words, the BVE method only works for large unit cells (see Fig. 2.3.1.2). A potential concern on all upper bound results is that they are influenced too much by fibers contacting the boundary conditions. It would be a simple matter to artificially force all fibers sufficiently far from the mesh edges. This approach, however, would effectively create a parallel structure that would degenerate to the lower bound results and therefore be far below experimental results. The better solution is to verify the volume element in BVE calculations is sufficiently large and this size requirement may be much higher then the size needed when using periodic RVEs with periodic boundary conditions.

Lastly, we comment on rectangular vs. elliptical fibers for the parallel structure. The modulus with a rectangular fiber was always very close to the modulus with an elliptical fiber (as seen by solid and dashed lines in Fig. 2.3.2.3). Looking closer, the elliptical fiber was always slightly stiffer than a rectangular fiber, with the exception of $R \leq 10$ and $\rho < 50$. Steif and Hoyson [22] previously looked at cylindrical vs. ellipsoidal fibers and saw larger differences, but they did different calculations. All their results were for the limit of low $V_f$ and they used different cylinder-ellipse analogies. Their calculations matched either minor or major axis of the ellipse to the corresponding axis of the cylinder and then either kept $\rho$ or $V_f$ constant. We claim our analogy with both $\rho$ and $V_f$ constant is more appropriate, although it non-intuitively leads to both the major and minor axes of the ellipse being larger than the fiber length and diameter, respectively. Although rectangular and elliptical fibers gave nearly the same modulus, they gave different fiber stress states. As known from Eshelby, the stress in an elliptical fiber is constant [2].
In contrast, a rectangular fiber shows classic stress transfer with low stress on the ends building to higher stress in the middle. These differences apparently do not affect modulus calculations, but they would be expected to affect models of composite properties that depend on fiber stress, such as modeling of stress transfer or interfacial failure.

2.3.3 Can an analytical model sufficiently capture the results of small periodic RVE composites?

Most analytical models consider a parallel structure with the single fiber geometry in Fig. 2.3.2.2 subjected to constant axial stress in the $y$ direction. Figure 2.3.2.3B shows numerical calculations for the single-fiber unit cell and compares to BVE lower bounds. The numerical calculations used constant traction in the $y$ direction rather then periodic displacement (i.e., the same boundary conditions used in analytical modeling). The numerical results were found to match lower bound results for all values of $V_f$, $\rho$, and $R$ that were studied. Furthermore the modulus for rectangular and elliptical fibers were nearly identical (the solid and dashed lines in Fig. 2.3.2.3B overlap). The next task was to see if analytical modeling reproduces numerical RVE results and thereby inherits agreements with lower bound BVE results, but also disagreements with upper bound BVE results for high $R$.

We first considered an Eshelby analysis [2], but all prior Eshelby models are for 3D composites with ellipsoidal fibers [1, 23] where we need a 2D analysis to compare to 2D FEA. Fortunately, the 2D, plane-strain results can be derived as outlined in the Appendix. Although an Eshelby analysis is for low $V_f$, that limit can be removed by a Mori-Tanaka extension. Tucker and Liang [9] point out that a Mori-Tanaka extension can be derived from an Eshelby analysis [2] by replacing the Eshelby tensor, $S$, with an effective
tensor, $\mathbf{S}^*$, defined by:

$$
\mathbf{S}^* = (1 - V_f)\mathbf{S} \tag{2.3.11}
$$

In addition to an Eshelby/Mori-Tanaka model (E/MT), we also compared to shear-lag methods. The common shear-lag solution in the literature [4, 5] and in textbooks [24, 25] considers two concentric cylinders (or two parallel layers when in 2D) with zero stress on the fiber ends. We tried this model (using optimal shear-lag parameters [4, 5, 6, 7]) and it was inaccurate. For a better analysis, we derived a new shear lag model for a single fiber encapsulated in matrix (i.e., the geometry in Fig. 2.3.2.2A). In addition, the new analysis accounts for stress transfer on the fiber ends and imperfect interfaces between the fiber and the matrix [7, 26]. This model, denoted as a shear-lag capped model (SLC), is derived next followed by comparison of E/MT and SLC to numerical calculations on the same structure and boundary conditions.

The SLC model is based on recently optimized shear lag methods that alter (and improve) the shear lag parameter [4, 5, 6] and explicitly account for imperfect interfaces [7]. The model is split into two regions (see Fig. 2.3.2.2A) and the $y$ axis is converted to a dimensionless coordinate using $\zeta = y/r_f$; the fiber top is at $\zeta = \rho$ and the matrix top is at $\zeta = \rho V_1/V_f$ where $V_1$ is fiber volume fraction within region II:

$$
V_1 = \frac{r_f L_{ft}}{r_m L_{ft}} = \frac{r_f}{r_f + \Delta} \tag{2.3.12}
$$

where $\Delta$ is found by Eq. (2.3.7). Region I is divided into two perfectly-bonded matrix layers aligned with the fiber — a “core” layer from $x = 0$ to $r_f$ and an “outer” layer from $x = r_f$ to $r_m$ (note that $V_1$ is also core layer volume fraction in region I). The general shear lag solution [5, 6, 7] for average axial stress in the core region is:

$$
\langle \sigma_c(\zeta) \rangle = \sigma_0 + C_1 e^{\beta_1 \zeta} + C_2 e^{-\beta_1 \zeta} \tag{2.3.13}
$$
where \( \sigma_0 \) is the total applied stress and \( \beta_1 \) is the shear lag parameter \([4, 5]\) in region I for layers with identical properties and a perfect interface:

\[
\beta_1^2 = \frac{3G_mV_1}{E_mV_2}
\]  

(2.3.14)

Here \( V_2 = 1 - V_1 \) is the matrix volume fraction in region II (and outer layer volume fraction in region I) and \( E_m \) and \( G_m \) are matrix tensile and shear moduli. Assuming uniform stress \( \sigma_0 \) along the edge at \( \zeta = \rho V_1/V_f \), using force balance, and redefining \( C_1 \), the average axial stresses in the region I layers simplify to:

\[
\langle \sigma_c(\zeta) \rangle = \sigma_0 + C_1 \sinh \left( \beta_1 \left( \zeta - \frac{\rho V_1}{V_f} \right) \right)
\]  

(2.3.15)

\[
\langle \sigma_o(\zeta) \rangle = \sigma_0 - \frac{C_1V_1}{V_2} \sinh \left( \beta_1 \left( \zeta - \frac{\rho V_1}{V_f} \right) \right)
\]  

(2.3.16)

In region II, the average axial stresses in the fiber and matrix are \([5, 6, 7]\):

\[
\langle \sigma_f(\zeta) \rangle = \sigma_\infty + C_3 \cosh(\beta_2 \zeta)
\]  

(2.3.17)

\[
\langle \sigma_m(\zeta) \rangle = \frac{\sigma_0 - V_1(\sigma_\infty + C_3 \cosh(\beta_2 \zeta))}{V_2}
\]  

(2.3.18)

where \( \sigma_\infty \) is the far-field fiber stress (i.e., stress at the middle of a long fiber) and \( \beta_2 \) is the shear lag parameter in region II \([7]\):

\[
\beta_2^2 = \frac{E_2V_1}{E_fE_mV_2} \frac{V_1}{3G_f} + \frac{V_2}{3G_m} + \frac{V_1}{r_fD_t}
\]  

(2.3.19)

where \( E_2 = E_fV_1 + E_mV_2 \) is rule of mixtures axial modulus of region II, \( E_f \) and \( G_f \) are tensile and shear moduli of the fiber, and \( D_t \) is an imperfect interface term. The imperfect interface is modeled by allowing interfacial displacement discontinuities that
are proportional to the traction in the displacement direction \[26\]. For region II, the axial displacement jump at \( x = r_f \) is \([w] = \tau(r_f)/D_t\), where \( \tau(r_f) \) is the interfacial shear stress. When \( D_t = \infty \), the displacement jump is zero and the interface is perfect; when \( D_t = 0 \), \( \tau(r_f) \) is zero and the interface is debonded; all other \( D_t \) values model an imperfect interface.

The two unknown constants, \( C_1 \) and \( C_3 \), can be eliminated by continuity conditions between the fiber end and the core layer in region I:

\[
\langle \sigma_f(\rho) \rangle = \langle \sigma_c(\rho) \rangle \quad \text{and} \quad [w(\rho)] = \frac{\langle \sigma_f(\rho) \rangle}{D_n} \tag{2.3.20}
\]

The first is stress continuity. The second is a new imperfect interface relation on the fiber ends where the jump in axial displacement between the fiber and the core layer is determined by \( D_n \), which is an imperfect interface parameter analogous to \( D_t \) but for normal displacements \[26\]. The displacement jump needed for this condition is calculated from

\[
[w(\rho)] = \Delta \langle w_m \rangle + \Delta \langle w_o \rangle - \Delta \langle w_c \rangle - \Delta \langle w_f \rangle \tag{2.3.21}
\]

where \( \Delta \langle w_i \rangle \) is the displacement difference between the top and bottom of region i. Using 1D Hooke’s laws:

\[
\Delta \langle w_m \rangle = r_f \int_0^\rho \left( \langle \sigma_m(\zeta) \rangle \frac{1}{E_m} + \alpha_m \Delta T \right) \, d\zeta \tag{2.3.22}
\]
\[
\Delta \langle w_f \rangle = r_f \int_0^\rho \left( \langle \sigma_f(\zeta) \rangle \frac{1}{E_f} + \alpha_f \Delta T \right) \, d\zeta \tag{2.3.23}
\]
\[
\Delta \langle w_c \rangle = r_f \int_{\rho}^{\rho V_1} \left( \langle \sigma_c(\zeta) \rangle \frac{1}{E_m} + \alpha_m \Delta T \right) \, d\zeta \tag{2.3.24}
\]
\[
\Delta \langle w_o \rangle = r_f \int_\rho^{\rho V_1} \left( \langle \sigma_o(\zeta) \rangle \frac{1}{E_m} + \alpha_m \Delta T \right) \, d\zeta \tag{2.3.25}
\]
where $\alpha_m$ and $\alpha_f$ are the thermal expansion coefficients of the matrix and fiber and $\Delta T$ is the temperature difference. Substituting the stresses, using

$$\sigma_\infty = \frac{E_f}{E_2} \sigma_0 + \alpha_2 \Delta T \quad \text{and} \quad \alpha_2 = \frac{\alpha_f E_f V_1 + \alpha_m E_m V_2}{E_2}$$

(2.3.26)

where $\alpha_2$ is the weighted rule-of-mixtures thermal expansion coefficient of region II, and integrating (in Mathematica, Wolfram Research) gives

$$[w(\rho)] = \frac{r_f \rho}{E_m V_2} \left[ 2C_1 \frac{\sinh^2(\beta^*_1 \rho)}{\beta_1 \rho} - C_3 \frac{E_2 \sinh(\beta_2 \rho)}{\beta_2 \rho} \right]$$

(2.3.27)

where

$$\beta^*_1 = \frac{(V_1 - V_f) \beta_1}{2V_f}$$

(2.3.28)

Solving Eq. (2.3.20) for $C_1$ and $C_3$ gives:

$$C_1 = \frac{\frac{\sigma_0}{T} \left( \frac{E_m V_2 \beta_1}{r_f D_m} + \frac{E_f \beta_1}{E_f \beta_2} \left(1 - \frac{\sigma_\infty}{\sigma_0} \right) \tanh(\beta_2 \rho) \right) \csch(\beta^*_1 \rho)}{\sinh(\beta^*_1 \rho) + \left( \frac{E_m V_2 \beta_1}{r_f D_m} + \frac{E_f \beta_1}{E_f \beta_2} \tanh(\beta_2 \rho) \right) \cosh(\beta^*_1 \rho)}$$

(2.3.29)

$$C_3 = \frac{\sigma_\infty \left( \frac{\sigma_0}{\sigma_\infty} - 1 \right) \sinh(\beta^*_1 \rho) - \frac{E_m V_2 \beta_1}{r_f D_m} \cosh(\beta^*_1 \rho) \sech(\beta_2 \rho)}{\sinh(\beta^*_1 \rho) + \left( \frac{E_m V_2 \beta_1}{r_f D_m} + \frac{E_2 \beta_1}{E_f \beta_2} \tanh(\beta_2 \rho) \right) \cosh(\beta^*_1 \rho)}$$

(2.3.30)

This stress state was compared to FEA average stresses and the results were good for a wide range of properties. Although this analysis assumed an isotropic fiber, it works for anisotropic fibers by replacing $E_f$, $G_f$, and $\alpha_f$ with the corresponding axial properties of an anisotropic fiber.

Finally, the modulus is found by integrating displacements in the outer matrix layers. By this process, the incremental length and effective modulus are:

$$\Delta L(\sigma_0, \Delta T) = \Delta \langle w_m \rangle + \Delta \langle w_o \rangle \quad \text{and} \quad \frac{1}{E^*} = \frac{2 \Delta L(\sigma_0, 0)}{\sigma_0 L_m}$$

(2.3.31)
Substituting stresses, $C_1$, and $C_3$ followed by much simplification (in Mathematica, Wolfram Research), the modulus can be cast as:

$$\frac{E_2}{E^*} = 1 + \left( \frac{E_f}{E_m} - 1 \right) (V_1 - V_f) + \frac{E_f V_f}{E_m V_m} \Lambda(\rho) \quad (2.3.32)$$

where

$$\Lambda(\rho) = \frac{V_m}{V_2} \frac{E_f \tanh(\beta_1 \rho)}{\beta_1 \rho} + \left( 1 + \left( 1 - \frac{E_f}{E_m} \right)^2 \frac{\tanh(\beta_1 \rho)}{\beta_1 \eta} \right) \frac{\tanh(\beta_2 \rho)}{\beta_2 \rho} \quad (2.3.33)$$

and $\eta = \frac{E_m V_2}{(r_f D_n)}$. In the limit of no region I ($V_1 \to V_f$) and debonded fiber end ($D_n \to 0$ and $\eta \to \infty$ to get zero stress on the fiber end), the stresses and modulus reduce to the standard shear lag result for two layers:

$$C_3 = -\sigma_\infty \text{sech}(\beta_2 \rho) \quad \text{and} \quad \frac{E_2}{E^*} = 1 + \frac{E_f V_f}{E_m V_m} \frac{\tanh(\beta_2 \rho)}{\beta_2 \rho} \quad (2.3.34)$$

The results here extend this old result to an encapsulated fiber including both fiber end stress transfer and an imperfect interface on fiber ends and sides.

Figure [2.3.3.1](#) compares E/MT and SLC models to numerical single-fiber unit cell (SFUC) models with traction loading and to lower bound BVE results for $R = 100$ or $R = 10^4$ and for $\rho = 5, 20,$ and 70. For both $R = 100$ and $R = 10^4$, both the SLC and E/MT models agreed well with both the SFUC and lower bound BVE. In summary, both the SLC and E/MT models accurately predict lower bound modulus for an aligned, short fiber composite for all tested values of $R$ and $\rho$. They track the lower bound because the models are based on an assumption of uniform far-field stress. Because upper and lower bound results are fairly close for $R \leq 100$, the SLC and E/MT models are also close to upper bound results within this range. But, for $R > 100$, these models should be recognized as providing pessimistic, lower bound modulus predictions.
Figure 2.3.3.1: Axial composite modulus for $R = 100$ (A) and $R = 10^4$ (B) as a function of fiber volume fraction for three fiber aspect ratios. The dashed and solid curves are analytical models based on the new shear lag method (SLC) and an Eshelby/Mori-Tanaka approach (E/MT), respectively. The dotted curves are numerical results with traction boundary conditions for a single-fiber unit cell (SFUC). The symbols are lower bound, Monte Carlo BVE results with error bars indicating their standard deviations.

There is a long history of refining analytical models for short fiber composites based on analysis of the single-fiber geometry [9]. Because the SLC and E/MT models agree with refined numerical models for lower bound modulus, this half of the problem is “solved,” leaving little room for seeking improved lower bound models. The development of better analytical models for upper bound modulus (e.g., using displacement boundary conditions) is tempting, but we claim is doomed to limited success. The best such analytical modeling could achieve would be to agree with numerical RVE results with periodic boundary conditions. Section 2.3.2 shows those results also give lower bound results for $R > 100$. In summary, future analytical modeling should focus on finding an upper bound modulus using non-unit-cell methods.
2.3.4 Can an analytical model account for 3D fibers and for imperfect interfaces?

Because analytical models agree with most lower bound BVE results and with upper bound BVE results for $R \leq 100$, we hypothesize that 3D analytical modeling would
agree similarly with 3D BVE modeling, even though the 3D BVE modeling is not available. This section compares 3D analytical modeling (an axisymmetric analysis), to numerical, axisymmetric, single-fiber unit cell results (which is the only unit cell amenable to axisymmetric analysis). In addition, this section investigates imperfect interface effects [7, 26]. Unfortunately, an Eshelby analysis [2] cannot be extended to modeling of imperfect interfaces. An Eshelby analysis works by exploiting the observation that elliptical fibers have constant stress; this property allows replacement methods to find modulus [11, 23]. When the interfaces are imperfect [26], however, the stresses in an elliptical fiber are no longer constant (as confirmed by FEA modeling), which means an Eshelby approach no longer works. In contrast, the SLC model derived above includes imperfect interfaces. This section therefore compares an axisymmetric SLC model to converged, axisymmetric FEA calculations with imperfect interface elements [27] to verify if the SLC model works in 3D and if it correctly models imperfect interfaces.

The SLC analysis in the previous section was for the 2D problem. It can easily be extended to an axisymmetric analysis for an end-capped fiber cylinder simply by redefining volume fractions, $\Delta$, and the shear lag parameters $\beta_1$ and $\beta_2$. The fiber volume fraction within region II becomes

$$V_1 = \frac{\pi r_f^2 L_f}{\pi r_m^2 L_f} = \frac{\rho r_f^2}{(r_f + \Delta)^2}$$  \hspace{1cm} (2.3.35)
where $\Delta$ is found by solving the following cubic equation

$$V_f = \frac{\pi r_f^2 L_f}{\pi r_m^2 L_m} = \frac{\rho r_f^3}{(r_f + \Delta)^2(\rho r_f + \Delta)}$$  \hspace{1cm} (2.3.36)

The shear lag parameters become \[7\]:

$$\beta_1^2 = -\frac{4G_m V_2}{E_m(V_2 + \ln V_1)} \quad \text{and} \quad \beta_2^2 = \frac{4E_2}{2G_f} - \frac{1}{E_m} \left( \frac{V_2}{V_1} + 1 + \frac{\ln V_1}{V_2} \right) + 2\frac{V_2}{r_f D_t}$$  \hspace{1cm} (2.3.37)

After these changes, all other equations in the SLC model are the same.

Figure 2.3.4.1 compares SLC models to FEA analysis of an axisymmetric model using periodic displacement or traction boundary conditions as a function of interface parameter for three different aspect ratios, two $R$ values, and all for $V_f = 0.15$. In these calculations, the two interface parameters were made equal $D_n = D_t$ and high values on the right correspond to the perfect interface limit. The SLC model accurately reproduces the numerical results and therefore provides a useful model for studying both 3D (cylindrical fibers) and imperfect interface effects. The SLC model falls between numerical results with displacement and traction boundary conditions and is closer to the traction results. This trend is likely because the SLC model is based on traction boundary conditions. Because an Eshelby analysis \[2\] cannot account for imperfect interfaces, it is plotted on the right as short, dashed horizontal lines representing the 3D (ellipsoidal fibers), perfect-interface, E/MT result \[1\] \[2\] \[23\]. Contrary to the Russel \[23\] approach of approximating the Eshelby tensor for high aspect ratio fibers, these calculations used the exact Eshelby tensor for ellipsoidal inclusions given in Ref. \[2\]. The Eshelby analysis is inconsistent. It is below numerical results for $\rho = 5$, but moves above it as $\rho$ increases.
Figure 2.3.4.1: Axial composite modulus for $V_f = 0.15$ as a function of fiber/matrix imperfect interface parameter and for three fiber aspect ratios. The open and solid symbols are upper and lower bound, axisymmetric, numerical calculations, respectively. The solid curves are axisymmetric version of the new shear lag solution. The dashed lines on the right are 3D Eshelby/Mori-Tanaka approach results for a perfect interface. Note that the $R = 10^5$ plot uses a log axis.

2.3.5 Other Properties

For mean field modeling of random or partially ordered composites, one needs all mechanical properties of the unit cell with random, aligned fibers. Most work focuses on analysis for $E^{(r)}_{yy}$ because it is the property that is most affected by fiber aspect ratio, $\rho$. Christensen [1] shows that for an Eshelby [2] analysis, the shear modulus is independent of $\rho$ and therefore equal to the shear modulus of a continuous fiber composite. Similarly, the transverse modulus, $E^{(r)}_{xx}$, and Poisson’s ratio, $\nu_{yx}$, may only weakly be affected by $\rho$. In other words, once $E^{(r)}_{yy}$ is found, the remaining properties are assumed to follow by simpler methods. We checked this conventional wisdom with the numerical BVE results. Figure 2.3.5.1 plots $E^{(r)}_{xx}$, $G^{(r)}_{xy}$, and $\nu^{(r)}_{yx}$ as a function of $\rho$ for two $R$ values and all for $V_f = 0.2$. For $R = 100$, all these properties are nearly independent of $\rho$ and thus are equal to results for continuous fiber composites. In contrast, for $R = 10^5$, $E^{(r)}_{xx}$ and $G^{(r)}_{xy}$ decrease. This behavior will need to be included when doing mean field modeling of such
Figure 2.3.5.1: Plots of $E_x^{(r)}$, $G_y^{(r)}$, and $\nu_y^{(r)}$ as a function of fiber aspect ratio for two $R$ values and all for $V_f = 0.20$. The dashed lines are for $R = 100$ and the solid lines are for $R = 10^5$.

2.4 Conclusions

This paper tackled seemingly basic questions whose answers, in our opinion, provide insights for evaluating past and future literature on short fiber composites. The novel results were to develop a method for bounding the mechanical properties and use that approach to study a regime that is not commonly examined (namely large $R$ and large $\rho$). The numerical experiments showed that for $R < 100$, the bounds are rather close and other numerical and analytical models fall within those bounds and therefore must be close to the correct answer. For $R > 100$, however, the numerical bounds diverge and both analytical methods and prior numerical methods based on periodic displacement boundary conditions degenerate to lower bound results. We do not claim the numerical upper bounds are predicting the modulus of real materials — they are upper bound results and because of the crude mesh are not the best upper bounds possible. But, all efforts to seek refined upper bounds suggest that at large $R$ even improved upper bounds are two or more orders of magnitude higher than results found by prior methods. Given that
some experimental results on reinforcement of elastomers [14, 16] exceed predictions by analytical or prior numerical models, but do not exceed upper bound BVE results, the two options are that current modeling methods are inadequate or that we must abandon continuum mechanics. The upper bound results here demonstrate the answer might be the former.

Analytical models typically treat a single fiber. The Eshelby/ Mori-Tanaka approach [2, 3] and the new shear lag method presented here, agreed well with lower bound, numerical, single-fiber models, but gave no information about upper bound modulus for high $R$. The new shear lag method adds modeling for imperfect interfaces. It is not worth the effort to seek “improved” analytical models because there is little room to improve agreement with numerical modeling on the same structure. The more interesting problem is how to avoid degenerating to a lower bound results. The next tasks for short fiber composite modeling should be to develop a new approach to analytical modeling that can predict upper bound moduli for all values of $R$ and to extend that modeling to composites with non-aligned fibers by averaging over a fiber distribution function [1].

2.5 Appendix

A 2D, plane-strain Eshelby analysis [2] can be derived by following Christensen [1], which is based on Russel [23]. We begin by specifying $\varepsilon_{11} = \varepsilon_0$, $\varepsilon_{22} = \varepsilon_r$, and $\varepsilon_{33} = 0$, where the fiber is the 1 direction and the 3 direction is the thickness direction with zero strain for a plane-strain analysis. Modifying Russel [23] with a plane-strain constitutive law and requiring only the stress in the 2 direction to be zero, the effective fiber direction
modulus and Poisson’s ratio become:

\[ E_{11}^* = E_m^{(r)} \left( 1 - V_f (A_{1111} - A_{1122} \nu_{12}^{*}) \right) \quad \text{and} \quad (2.5.1) \]

\[ \nu_{12}^* = \frac{\nu_m^{(r)} - V_f (A_{2211} + \nu_m^{(r)} A_{1111})}{1 - V_f (A_{2222} + \nu_m^{(r)} A_{1122})} \quad (2.5.2) \]

where \( A_{ijkl} \) are elements of the fourth-rank tensor that relates Eshelby transformation strain to applied strain:

\[ \varepsilon_{ij}^T = A_{ijkl} \varepsilon_{kl}^0 \quad (2.5.3) \]

Continuing along a 2D plane-strain analog of the Russel analysis [23], the \( A_{ijkl} \) terms can be found from

\[ A_{1111} = \frac{a_{22} b_{11} - a_{12} b_{12}}{a_{11} a_{22} - a_{12} a_{21}} \quad A_{1122} = \frac{a_{22} b_{12} - a_{12} b_{22}}{a_{11} a_{22} - a_{12} a_{21}} \quad (2.5.4) \]

\[ A_{2211} = \frac{a_{11} b_{12} - a_{21} b_{11}}{a_{11} a_{22} - a_{12} a_{21}} \quad A_{2222} = \frac{a_{11} b_{22} - a_{21} b_{12}}{a_{11} a_{22} - a_{12} a_{21}} \quad (2.5.5) \]

where

\[ a_{11} = \Delta \lambda (S_{1111} + S_{2211}) + 2 \Delta G S_{11111} + \lambda_m + 2 \lambda_m \quad (2.5.6) \]

\[ a_{12} = \Delta \lambda (S_{1122} + S_{2222}) + 2 \Delta G S_{11222} + \lambda_m \quad (2.5.7) \]

\[ a_{21} = \Delta \lambda (S_{1111} + S_{2211}) + 2 \Delta G S_{2211} + \lambda_m \quad (2.5.8) \]

\[ a_{22} = \Delta \lambda (S_{1122} + S_{2222}) + 2 \Delta G S_{22222} + \lambda_m + 2 \lambda_m \quad (2.5.9) \]

\[ b_{11} = b_{22} = -\Delta \lambda - 2 \Delta G = -(\lambda_f - \lambda_m) - 2 (G_f - G_m) \quad (2.5.10) \]

\[ b_{12} = b_{21} = -\Delta \lambda = -(\lambda_f - \lambda_m) \quad (2.5.11) \]

and \( S_{ijkl} \) are elements of the 2D, plain-strain Eshelby tensor. The terms \( \lambda_f \) and \( \lambda_m \) are the Lamé parameters for the fiber and matrix. For results, Russel [23] substituted the 3D Eshelby tensor [2] (as approximated for large aspect ratio [1, 23]) and took limiting results
for small $V_f$. Here we need the 2D plane-strain Eshelby tensor [2] evaluated exactly to handle small aspect ratios and we used the full modulus and Poisson’s ratio expressions instead of their low $V_f$ limits. Fortunately, Eshelby [2] provides explicit 2D plane-strain results for the case with elliptical axes $a > b$ ($\rho = a/b$) and $c = \infty$:

\[
S_{1111} = \frac{1}{2(1 - \nu_m)} \left( \frac{1 + 2\rho}{(\rho + 1)^2} + \frac{1 - 2\nu_m}{\rho + 1} \right) 
\]

(2.5.12)

\[
S_{1122} = \frac{1}{2(1 - \nu_m)} \left( \frac{1}{(\rho + 1)^2} - \frac{1 - 2\nu_m}{\rho + 1} \right) 
\]

(2.5.13)

\[
S_{2211} = \frac{1}{2(1 - \nu_m)} \left( \frac{\rho^2}{(\rho + 1)^2} - \frac{(1 - 2\nu_m)\rho}{\rho + 1} \right) 
\]

(2.5.14)

\[
S_{2222} = \frac{1}{2(1 - \nu_m)} \left( \frac{\rho(\rho + 2)}{(\rho + 1)^2} + \frac{(1 - 2\nu_m)\rho}{\rho + 1} \right) 
\]

(2.5.15)

Here $\nu_m$ is the unreduced matrix Poisson’s ratio and it is related to the plane-strain Poisson’s ratio by $\nu_m = \nu_m^{(r)}/(1 + \nu_m^{(r)})$.

Bibliography


To raise new questions, new possibilities, to regard old problems from a new angle, requires creative imagination and marks real advance in science.

Albert Einstein

Solution map for prediction of upper and lower bound stiffness of nanocomposites

Complex and unknown behaviors of nanoscale materials necessitate multi-scale modeling approach to predict and describe their properties. In multi-scale approach, computational modeling of materials can be divided in two categories; computational chemistry and continuum mechanics [1]. On one hand, nanoscale materials may interact at the atomic level where continuum mechanics does not apply, and the behavior of materials depends on these interactions. For instance, in polymer nanocomposites, bond strength, inter-
molecular interaction, bond rotation, and more affect the properties of nanocomposite and these relate to intrinsic structure of materials that might be best addressed and the molecular level using computational chemistry (e.g., molecular statics and dynamics, coarse graining) [1, 2, 3, 4, 5, 6]. On the other hand, measurement of material properties and applications at the macro scale, where the behaviors only can be explained by having a representative volume element (RVE) based on continuum mechanics. An example of these properties is elasticity. Methods that account for fundamental theories of mechanics are established as micromechanics or finite elements and more [1, 2, 7, 8, 9].

3.1 Introduction

The challenge of this scheme (multi-scale modeling) is connecting these two categories together to predict properties that are comparable with experimental data [1, 7, 10, 11]. The next step, for predicting properties of nanoscale materials, is to have an analytical model with well-established theories that can reproduce the same results as computational models. Analytical models are desirable because computational models are expensive, time consuming [7, 9], and sometimes not accessible for researchers. Here, we focus on mechanical properties of nanocomposites, specifically change in stiffness with addition of nanoparticles to a polymer matrix.

One of the uses of nanoscale materials is to increase mechanical properties of polymers nanocomposites [12, 13, 14]. The general goal is to increase these properties with addition of low volume fraction ($V_f$) of nanoparticles. Some literature has reported drastic increase in mechanical properties of composites with addition of low $V_f$ of nanoscale particles, which was not achievable with the same particles at micro or macro scales [8, 9, 15, 16, 17]. In atomic scale, existence of functionized nanoparticles can change the structure and properties of the host matrix (e.g., crystal structure, crystallinity and more)
Although experimental results qualitatively prove existence of an interface layer (interphase) between nanoparticles and matrix [19, 20, 21, 22] quantitative measurement of these layers are lacking [1, 8].

In finite element analysis (FEA) methods, to model these nanocomposites, some literature suggested introducing an unknown interphase layer with an arbitrary volume fraction and properties for interphase layer to fit the experimental data [8, 9] as a hybrid numerical-analytical method to predict the mechanical properties of nanocomposite [9]. Although this approach is reasonable for nanocomposites with available experimental data, it only works for a narrow selection of nanocomposites. Models that can cover wider range of nanocomposites are more convenient to predict the properties. There are several analytical models that have been used to predict stiffness on nanocomposite with addition of nanoparticles [23]. Computational methods are a useful tool to validate these analytical models [7]. Then, analytical models can be used to compare experiments with theories.

In previous work, [7] we used a numerical model (Monte Carlo FEA) to show that the most accepted analytical models in micromechanics community (Mori Tanaka (MT) and modified Shear-Lag) predict pessimistic stiffness results for rubbery nanocomposites and underestimate their properties. Also, we introduced the Shear-Lag-Capped (SLC) model, a developed and more accurate [7] version of Shear-Lag (SL) models, which are analytical models for stiffness prediction of short fiber composites [24, 25, 26, 27]. Furthermore, We showed that the SLC as the only analytical model that counts for imperfect interface between fiber and matrix in composites, predicts similar results to finite element analysis (FEA) [7].

But SLC only works for nanocomposite with low stiffness mismatch ($R = \frac{E_f}{E_m} \leq 100$) of nanoparticle ($E_f$) and matrix ($E_m$). Also, all simulations and results that were dis-
discussed in previous work, like most of short fiber analytical models, was for unidirectional short fiber composites [7]. In real life, fibers (nanoparticles) in nanocomposites are either randomly oriented or partially aligned [28, 29]. Once the properties of unidirectional aligned composite is known (elastic properties of unit cell), we can use mean field theory as described elsewhere [29, 30] to predict properties of randomly oriented or partially aligned nanocomposites. In the present work, we shall use Monte Carlo FEA results [7] to introduce an analytical (for $R < 70$) and a hybrid analytical-numerical (for $R > 70$) model, for the stiffness prediction, that covers a broader range of nanocomposites.

3.2 Methods

All simulations were plain strain with with 8-node quadrilateral elements were done using the open source code NairnFEA [31]. The computational experiments were done for different fiber volume fractions ($V_f = 0.01, 0.02, 0.05, 0.1, 0.15, 0.2, \text{ and } 0.25$), fiber aspect ratios ($\rho = 5, 10, 20, 40, 70, 100 \text{ and } 150$), and fiber to matrix modulus ratios ($R = 10, 100, 1000, 10^4, \text{ and } 10^5$). Young’s modulus of fibers in all simulations were 100 GPa, and for different $R$ values, matrix modulus was changed. Monte Carlo FEA was generated by using script control (20 replicates for each combination of $\rho, V_f, \text{ and } R$), to account for the random distribution of aligned short fiber composite structures. Figure 3.2.0.1 shows examples of aligned short fiber composites that we ran (Monte Carlo FEA). Simulations were run with two boundary conditions; Fixed displacement in both directions along fibers and perpendicular (which was called BVE in previous work [7]) for upper bound) and fixed stress along fibers (lower bound) as it was explained elsewhere [7](see Fig. 3.2.0.1). The average and the standard deviation of modulus were used to compare with analytical models. In a sense, In upper bound (BVE), fibers interact and lock each other (and lock matrix) from moving and in lower bound, fibers act independently from
3.3 Results and Discussion

3.3.1 Finding the properties of unit cell

For randomly oriented (or partially aligned) nanocomposites, we need to average the properties of a unit cell over all directions [30]. Unit cell is the smallest cell that can represent the whole composite. Averaging elastic properties (stiffness or compliance tensor) of composites, in 3D, needs five independent variable from stiffness (or compliance) tensor of unit cell (assuming unit cell is transversely isotropic) [7, 30, 32]. These variables are Young’s modulus of unit cell along fiber ($E_A$), Young’s modulus of unit cell in transverse direction ($E_T$), in-plane and our-of-plane Poisson’s ratio ($\nu_A$ and $\nu_T$), and in-plane shear modulus ($G_A$) of unit cell. For 2D (plane strain) averaging we only need 3 variables ($E_A$, $E_T$, and $G_A$). Theoretical and numerical results show that $E_A$ significantly depends on aspect ratio of fibers (or particles), and the other properties can therefore be
found from simpler theories for unidirectional continuous-fiber composites\cite{7,32}.

In brief, our strategy is to use SLC solution, find a unit cell that can generate the same results as Monte Carlo FEA (as a simulation of aligned short fiber nanocomposites), and then use the mean-field averaging to predict the properties on randomly oriented (or partially aligned) nanocomposites which happens in real experiments (see Fig. \ref{fig:3.3.1.1}).

We shall use SLC (with imperfect interface) only for $E_A$ and other variables are similar to continuous-fiber composites \cite{7,32} (with imperfect interface) and calculated as described elsewhere \cite{30}. SLC explicitly includes imperfect interfaces and stress transfer on the fiber ends (see Fig. \ref{fig:3.3.1.1} (b)). It has two interface parameters that account for imperfect interface (or interphase); $D_t$ and $D_n$. These two parameters allow displacement discontinuities in displacement direction. When $D_t$ (or $D_n$) = 0, the interface is debonded, the interface is perfect; when $D_t$ (or $D_n$) = $\infty$; all other $D_t$ and $D_n$ values model an imperfect interface \cite{7,30}.

These two parameters can be measured by experiment \cite{33,34}, or by fitting the model to experimental results \cite{23,35} or MD simulations \cite{1,2,9,35}. In previous work, we showed SLC results (as a unit cell) is almost identical to Monte Carlo FEA for aligned short fiber nanocomposites with low $R$ (\textit{e.g.}, nanocomposites with glassy matrix where $R$ is $< 100$). As $R$ increases, lower bound (LB) and upper bound (UB) get far apart (high $R$ refers to nanocomposites with low stiffness matrix and high stiffness nanoparticle).

For nanocomposites with high $R$ value, SLC model predicts lower bound Monte Carlo FEA results, as it is expected, because SLC and lower bound have the same boundary conditions (both assume uniform far-field stress) \cite{7}. To overcome this gap, we shall reconsider fiber effectiveness that has been used in text books citeHull:1996.

$$E_c^{UB} = (1 - V_f)E_m + \eta_f E_f V_f$$ (3.3.1)
Figure 3.3.1.1: Three steps on evaluation of SLC as an analytical model for nanocomposites; Using upper bound and lower bound Monte Carlo FEA results as a simulation of aligned nanocomposite (a); then using Shear-lag-capped unit cell solution to fit with Monte Carlo FEA, and reproduce the same result (b); and last, use Mean-field Averaging for stiffness prediction of randomly oriented (or partially aligned) nanocomposites (c).

where $E_m$, $V_f$, and $\eta_f$ are young’s modulus of matrix, volume fraction of nanoparticles and fiber effectiveness respectively. $\eta_f$ varies from 0 to 1 where 0 means no stiffness from nanoparticles (act as voids) and 1 is for unidirectional continuous-fiber composite. Fiber effectiveness ($\eta_f E_f$) compare average stress in the fiber to the stress the fiber would have in a continuous fiber composite:

$$\eta_f^{UB} = \frac{1}{l_f \sigma_\infty} \int_{-l_f/2}^{l_f/2} \langle \sigma_{yy,f}^{EC} \rangle dy$$  \hspace{1cm} (3.3.2)$$

Here $l_f$ is fiber length, $\sigma_\infty$ is stress that would be in an infinitely long fiber, and $\langle \sigma_{yy,f}^{EC} \rangle$ is average stress in the fiber cross section at position $y$. Fiber effectiveness is an optimistic model for short fiber composite and give an “upper bound” for short fibers. Since, most of nanoparticles have high aspect ratios ($\rho$), a combination of $E_{EC}$ and $E_{cLB}$ is more realistic
for nanoparticles:

\[ E^* = \phi_L E_{EC} + (1 - \phi_L) E_{UB} \quad (0 < \phi_L < 1) \quad (3.3.3) \]

where \( E^* \) is the nanocomposite young’s modulus (with aligned fibers). The axial modulus from the end-capped model, \( E_{EC} \) was derived to be [7]:

\[
\frac{E_2}{E_{EC}} = 1 + \left( \frac{E_f}{E_m} - 1 \right) (V_1 - V_f) + \frac{E_f V_f}{E_m V_m} \Lambda(\rho) \quad (3.3.4)
\]

where \( E_i \) is modulus and \( V_i \) is volume fraction. Subscripts \( f \) and \( m \) refer to fiber and matrix, but \( V_1 = r_f^2/r_m^2 \) is volume fraction on fiber ignoring the end caps and \( E_2 = E_f V_1 + E_m (1 - V_1) \). The key function of aspect ratio \( (\rho) \) was derived to be:

\[
\Lambda(\rho) = \frac{V_m \frac{E_2}{E_f} \tanh(\beta^*_1 \rho)}{V_2} + \left( 1 + \frac{E_2}{E_f} \right)^2 \frac{\tanh(\beta^*_1 \rho)}{\beta^*_1 \eta} \frac{\tanh(\beta_2 \rho)}{\beta_2} \quad (3.3.5)
\]

where \( \beta^*_1 = (V_1 - V_f) \beta_1/(2V_f) \), \( \eta = E_m V_2/(r_f D_n) \),

\[
\beta_1^2 = -\frac{4G_m V_2}{E_m (V_2 + \ln V_1)} \quad \text{and} \quad \beta_2^2 = \frac{1}{2G_f} - \frac{V_2}{G_m} \left( \frac{V_2}{2} + 1 + \frac{\ln V_1}{V_2} \right) + \frac{2V_2}{r_f D_t} \quad (3.3.6)
\]

Using SLC model for find fiber effectiveness with imperfect interfaces gives:

\[
\eta_f = 1 - \frac{1 + \left( 1 - \frac{E_2}{E_f} \right) \frac{\tanh(\beta^*_1 \rho)}{\beta^*_1 \eta} \frac{\tanh(\beta_2 \rho)}{\beta_2 \rho}}{1 + \frac{\tanh(\beta^*_1 \rho)}{\beta^*_1 \eta} + \frac{E_2}{\eta E_f} \frac{\tanh(\beta_2 \rho)}{\beta_2 \rho}} \quad (3.3.7)
\]

Here we compare \( E^* \) with Monte Carlo results tho find \( \phi_L \) value for different \( R \) and \( \rho \).

Figure 3.3.1.2(a) shows solution map for regenerating Monte Carlo FEA upper bound.
Figure 3.3.1.2: Solution map for regenerating aligned short fiber Monte Carlo FEA (BVE) upper bound results using SLC unit cell with $\phi_L$.

using SLC fiber effectiveness (with $\phi_L$). Clearly, $\phi_L$ is a function of $R$ and $\rho$. For Low $R$ values ($R < 60 - 70$), UB and LB Monte Carlo FEA were close and $\phi_L$ is one (green zone in Fig. 3.3.1.2(a)). As $R$ increases, $\phi_L$ decreases and fiber effectiveness is a mixture of UB and LB. For High $R$ values, $\phi_L = 0.93$ generates Monte Carlo FEA results ($\eta_f$ is bounded with $7\% \eta_f^{UB}$ and $93\% \eta_f^{LB}$), which is yellow zone in solution map. And for the other ranges (red zone), $\phi_L$ is between 0 to 1 and is found by interpolation (see Tab. 3.1 in appendix for different $\phi_L$ in red zone). Figure 3.3.1.2(b) shows a 3D map of fitting SLC, to reach Monte Carlo FEA upper bound.

Figure 3.3.1.3 shows results of $E_A$ vs. $V_f$ for different $R$ and $\rho$ values based on solution map. For $R = 10$, SLC matches upper bound (BVE) results of all aspect ratios (only $\rho = 20$ is shown in the plot) because upper bound and lower bound results are close when $R$ is small [7]. Generally, in all aspect ratios and $R$ values, SLC with $\phi_L = 1$ (dashed lines) only matches lower bound Monte Carlo FEA (circle symbols connected with dashed lines), and when bounds get far apart (higher $R$ value) $\phi_L$ changes. For $R = 10^5$, using $\phi_L = 0.93$ results match with upper bound BVE (see Fig. 3.3.1.3). This can be explained when the matrix has very low stiffness ($R \rightarrow \infty$) the maximum possible upper bound fiber efficiency ($\eta_f^{UB}$) is 7 % regardless aspect ratio (assuming the interface
is perfect). But for instance when \( R = 100 \), with increasing \( \rho \), \( \phi_L \) changes from yellow zone to red zone of solution map (see Fig. 3.3.1.2 and 3.3.1.3 (A)). For \( R = 10^3 \) and \( 10^4 \) also, \( \phi_L \) varies with \( R \) and \( \rho \), to match upper bound BVE (see Fig. 3.3.1.3 (B) and (C)).

### 3.3.2 Mean-field averaging

Here, we use SLC (with solution map) as unit cell. We imagine the nanocomposite as made up of mini nanocomposites with the fibers in the axial direction (see Fig. 3.3.1.1 (c)). By applying constant strain (\( \varepsilon_0 \)) or constant stress (\( \sigma_0 \)), the upper and lower bound modulus are calculated receptively by integrating properties in all directions using eq. 3.3.8.

\[
\Pi = \int_V \Pi(\theta, \phi) P(\theta, \phi) d\theta d\phi
\]  
(3.3.8)

Where \( \Pi \) is modulus in each direction, \( P \) is oriented distribution function (ODF) \([18]\) of fibers and \( V \) is the volume of composite. Details about the ODF and partially aligned nanocomposites can be find elsewhere \([18]\) (also see Ch. 6). For randomly oriented composites \( P \) is constant (\( \frac{1}{4\pi} \)), and \( \Pi \) is constant in all directions. Integrating over all angles, for upper bound (when \( \varepsilon_0 \) is applied):

\[
E_c = 4U_2(1 - \frac{U_2}{U_1}) \quad \text{and} \quad G_c = U_2
\]  
(3.3.9)

Where:

\[
\begin{align*}
U_1 &= \frac{3E_A + 3E_T + 4G_A + 2E_A \nu'_A - 4G_A \nu'_A}{8 - 8\nu_A \nu'_A} \\
U_2 &= \frac{E_A + E_T + 4G_A + 2E_A \nu'_A - 4G_A \nu'_A}{8 - 8\nu_A \nu'_A} \\
\nu'_A &= \nu_A \frac{E_T}{E_A}
\end{align*}
\]
Figure 3.3.1.3: $E_A$ vs. $V_f$ plots for different $R$ and $\rho$ values. The symbols (with error bars) are upper bound and lower bound Monte Carlo FEA (BVE) results, and colors are similar to solution map; blue color is representing lower bound BVE results ($\circ$), green color are where SLC matches BVE upper bound using $\phi_L = 1$, yellow for the area with $\phi_L = 0.93$ and other colors for the red zone in solution map (interpolation for $\phi_L$). Dashed line are SLC results and solid line SLC with different $\phi_L$ showed on plots ($\phi_L$ is 0.93 (yellow) if it is not showed on solid lines). (A) is for $R = 10$ and 100, and (B) for $R = 1000$. (C) Only upper bound results are shown;The symbols (with error bars) are upper bound Monte Carlo FEA (BVE) results, and colors are similar to solution map; Yellow is for the area with $\phi_L = 0.93$ and other colors for the red zone in solution map (interpolation for $\phi_L$), and solid line SLC with different $\phi_L$ showed on plots ($\phi_L$ is 0.93 (yellow) if it is not showed on solid lines). (D) The symbols (with error bars) are upper bound (triangle and square) and lower bound (circle) Monte Carlo FEA (BVE) results. Dashed line are SLC results using $\phi_L = 1$, and solid line SLC with $\phi_L = 0.93$. 
And for lower bound (when $\sigma_0$ is applied):

$$E_c = 8\left(\frac{3}{E_T} + \frac{1}{G_A} + \frac{3 - 2\nu_A}{E_A}\right)^{-1} \quad \text{and} \quad G_c = 2\left(\frac{3}{E_T} + \frac{1}{G_A} + \frac{1 - 2\nu_A}{E_A}\right)^{-1} \quad (3.3.10)$$

Figure 3.3.2.1, fig:LDPE-CNC and 3.3.2.3 show $E_c$ vs. $V_f$ results, from different experiments [36, 37, 38, 39, 40, 41] comparing with different analytical models. Experiment were chosen to compare all three zones of solution map results (green, red yellow).

It should be noted that beside SLC with solution map, we compared Mori-Tanaka (MT) and Halpin-Tsai (HT) models (two analytical models that are used commonly for stiffness prediction of nanocomposite) with experiments. More details about analytical models for nanocomposites and their limitations can be found elsewhere [23].

In Fig. 3.3.2.1 experiments (polyamide reinforced with carbon nanotube) are below the models ($R \sim 70$, green zone in SLC solution map). Here, using $\phi_L = 1$ and $D_t = D_n = 0.6 \left(\frac{kPa}{nm}\right)$ for SLC fits the experiments. Some literature suggested to use a modified HT [42] or MT [35] for specific nanocomposites to calculate effective properties of nanoparticles. Their approach is to use a fraction of MT or HT to fit experiments (account for random orientation and interface in the used fraction) and only is calculated for the used specific nanocomposites. This is similar to fiber effectiveness in SLC, which depend on interface, aspect ratio and orientation. Our approach, SLC model, covers wider range of nanocomposites.

Figure 3.3.2.2(A) shows results low density poly ethylene (LDPE) reinforced with tunicate cellulose nano crystals (CNC) [40]. $R$ value is around 300 and $\rho$ is 84 (experiment falls in red zone of solution map). Experiment exceed HT model (red line) and shows almost perfect interface ($D = \infty$) if we use $\phi = 1$ for SLC (dotted line), which means we have maximum possible reinforcement in this nanocomposite. But, based on solution map, $\phi$ should be around 0.75 (dash-dot line in Fig. 3.3.2.2(A)), and using imperfect
interface \( (D_t = D_n = 0.1 \ \frac{MPa}{nm}) \), SLC fits the experiments better than other models.

Figure 3.3.2.2 (B) is another experiment from literature [41]. The experiment was on Poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP) reinforced with wood pulp CNC \((R \text{ value around 250-300 and } \rho \text{ 16-18, which is in yellow zone of solution map})\). Again, Experiments exceed HT (red line) and traditional SLC \((\phi = 1)\) but using 0.93 for \(\phi\) (dash-dot line) predicts that higher stiffness is achievable with better interface (solid line shows SLC with \(\phi = 0.93\) and \(D_t = D_n = 0.5 \ \frac{MPa}{nm}\)). The difference between Fig. 3.3.2.2 A and B is that the aspect ratio of CNC is smaller in B with makes the experiments fall in yellow zone. Furthermore, SLC fits with experiment at higher interface value, which could be an indication of better compatibility with CNC (comparing LDPE and PVdF-HFP).

Figure 3.3.2.3 shows two different experiments as representation of rubbery nanocomposites \((R > 10^5 \text{ and different } \rho \text{ values})\) [36, 39]. As expected, in Fig. 3.3.2.3 (A) traditional models (HT, MT and SLC) underestimate the modulus of nanocomposites. But using \(\phi_L = 0.93\) predicts that stiffness could be potentially two order of magnitude higher than experiments if the interface was perfect between fiber and matrix.

In Fig. 3.3.2.3 (B), with addition of nanoparticles the interface modulus (that fits the
Figure 3.3.2.2: $E_c$ vs. $V_f$ for LDPE/CNC [40] (A) and PVdF-HFP/CNC (B).

Figure 3.3.2.3: $E_c$ vs. $V_f$ for Nanoclay/rubber (A) [39] and WPU/CNC (B) [36].

experiment) increases which can be an indication of change in the structure of polymer.

In the other word, SLC (and other analytical models) assume no change in the matrix structure but experiments show addition of nanoparticles could change the polymer matrix structure and this increase in interface modulus could be explained as more interface formation in composites as $V_f$ increases an overall modulus of composite (and interface) changes.

**Remarks:** SLC assumes the is no agglomeration in nanocomposites, and experiments show when nanoparticles agglomerate, mechanical properties drop (which in contrast to
percolation model). Also, agglomeration depends on geometry (aspect ratio) of nanoparticle and their compatibility with the host matrix. For instance, nanoparticles agglomerate at higher $V_f$ in more compatible matrix (comparing two different palymers reinforce with the same nanoparticles), which could be defined as better interface.

Analytical models assume no change in polymer matrix structure (e.g., crystal structure) with addition of nanoparticles in contrast to experiments (more details about other analytical models that are used for nanocomposites can be found elsewhere [23]. This gap are filled by interface parameters in SLC model which play an important role in reinforcement of matrix (with transferring the load from matrix to stiff nano particles). But needs more investigation on measurement of interface (thickness of interface and its properties), both experimental and simulation (computational chemistry). Analytical models derived with different physical assumptions based on mechanism of reinforcement, and it should be considered which one describes the physics of reinforcement in the composite. SLC, in our believe, describes the physics of reinforcement in nanocomposites better that others.

Here, in our calculations, we assumed $D_t$ and $D_n$ have the same value to simplify our calculations but they can have different values if it is confirmed by experiments. Also, SLC model assumes the nanoparticles have a fibrous shape. For nanoparticles with irregular shape, aspect ratio ($\frac{\text{length}}{\text{thickness}}$) and the thickness of particle could have similar definition using SLC model.

Advances in measurement science and computing technology provide tools for more accurate prediction of nanomaterials. For instance, here, Monte Carlo FEA was run inevitably with crude mesh due to computational limitations. Having more powerful computing technology could tune the boundary of solution map. Until then, SLC solution map could be a useful model to predict possibility of reaching desired stiffness in different nanocomposites.
3.4 Appendix

Table 3.1: $\phi_L$ value as a function of $R$ and $\rho$

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<td>10</td>
<td>20</td>
<td>40</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td>$\phi_L$</td>
<td>0.95</td>
<td>0.94</td>
<td>0.935</td>
<td>0.93</td>
<td>0.93</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Bibliography


It doesn’t matter how beautiful your theory is, it doesn’t matter how smart you are. If it doesn’t agree with experiment it’s wrong.

Richard P. Feynman

Stiffness prediction of nanocomposites:

Experimental evaluation of design models

The goal of this chapter is to evaluate analytical models that predict stiffness of nanocomposites. In 1959, Richard Feynman presented a topic about "There’s Plenty of Room at the Bottom", which he described manipulating materials at smaller scales [1]. Although he did not specifically mentioned nano scale materials, his presentation was a motivation for researchers. Today, nano scale materials are being used for wide variety of applications. One of the promising research areas for nano scale materials is for reinforcement
of different polymeric materials to reach desirable stiffness. Mostly, the stiffness of these materials are being found experimentally [2, 3, 4, 5] because nanocomposite community lacks decent analytical model that can provide reliable prediction.

4.1 Introduction

Numerical Methods (e.g., finite element analysis (FEA)) is an other option to predict properties, but they are usually expensive, time consuming and sometimes they have their own issues that need to be solved (e.g. meshing, convergence, and boundary conditions) [6, 7]. Analytical models would be preferable because once the mechanics is known, it is possible to substitute the initial properties of composite components and calculate the composite properties. Tremendous time/cost savings can be realized in the development of new products if design models allow accurate prediction of final properties based upon easily obtained initial parameters. However, there are currently few mathematical models that can be used to predict the properties of nanocomposite materials and those may only work in a few specific cases [6, 8, 9].

There are two different views about analytical modeling for mechanical properties of nanocomposites. The first common view is that the continuum mechanics does not apply to nanocomposites, but this view has not been backed up by facts. It is used to hype claims that nanocomposite will be great because new mechanics apply [ref]. This view has the obvious flaw that if there are new mechanics what are those mechanics and how can one claim those, new mechanics (when available) will not predict stiffness of nanocomposites to be worse than expected continuum methods instead of better? Until all assumptions in continuum mechanics have been considered, it cannot be claimed that continuum mechanics does not work for modeling stiffness of nanocomposites [6, 10][ref]. If experiments deviate from continuum mechanics models that have been independently validated as ac-
accurate, only then can one say new mechanics are needed. To jump to that conclusion based on intuition about sizes or based on use of inaccurate models is a poor approach.

The second view considers nanocomposites as short fiber composites, and therefore uses short fiber composite models with continuum mechanics methods to predict stiffness of different nanocomposites [6]. In order to model the stiffness of general composite materials, they should be divided in two categories due to the difference in the mechanism of reinforcement; continuous-fiber composites (see Fig.4.1.0.1(a)), in which, fibers carry load from end to end, and discontinuous-fiber or short fiber (see Fig.4.1.0.1(b)) composites where stress transfer into the fiber plays an important role in the properties.

In traditional composites, the ratio of fiber and matrix stiffness is usually small ($R = \frac{E_f}{E_m} \leq 40$) for both short-fiber and continuos-fiber composites [11][ref for continuos]. On the other hand, the $R$ value has a wide range for nanocomposites. Nanoparticles are being used for reinforcement polymers from high stiffness polymers ($R \sim 10$) to soft elastomers ($R \sim 10^6$) [6, 10]. Many existin models were developed for lower $R$ values and do not work well, despite their use, for high $R$ value composites.

The simplest way of predicting the composite stiffness is using a ”rule of mixtures”. But rule of mixture is only a very optimistic upper bound to properties. In real composites, the properties will always be lower dues to such things and misaligned fibers and stress transfer effects into short fibers [12]. Both these issues are important and short fiber composites meaning the mechanism of reinforcement is different [13][ref]. Since fibers carry load indirectly (matrix carries load end to end), reinforcement is more sensitive to the interface, aspect ratio of fibers [13] and the $R$ value [6]. In selecting models for consideration, we divide models to these two (continuous and discontinuous) categories, impose the limitations of each model and only use models that are based on short fiber composites.

Most of short fiber analytical models are for aligned fibers, and experimental results
are almost always for random or partially aligned fiber composites. Once the model is known (elastic properties of aligned fiber composite), we can use mean field theory as described by Shir Mohammadi and Nairn(2016) \cite{14, 15} to predict modulus over all directions (randomly oriented) and compare them with experiments and partially aligned nanocomposites as explained elsewhere \cite{16}. Since we are looking for the maximum achievable properties of composites, we only plot upper bound results of models in our plots. Furthermore, most of the models solve for stiffness or compliance tensors of composites, but here we will only discuss Young’s modulus of composites (which could be expanded to other elastic properties as needed).

4.2 Experiment Methods

Materials: Poly(methyl methacrylate) (PMMA) with molecular weight of \( M_w \) 75,000 and density of 1.18 gr.cm\(^{-3} \) was purchased from Scientific Polymer Products,
Inc., Polysulfone (PSf) with $M_w$ of 35,000 $D$ and density of 1.24 gr.cm$^{-3}$ was donated by Solvay Advanced Polymers (Alpharetta, GA). PVdF with the density of 1.78 gr.cm$^{-3}$ and ($M_w$) of 530,000 $D$ was purchased from Scientific Polymer products inc. NY, U.S.A. PVdF-HFP, with $M_w$ of 400,000 $D$ and density of 1.78 gr.cm$^{-3}$ was purchased from Aldrich Chemical Co. Dimethylacetamide (DMAc) was used as the organic solvent and it was purchased from Honeywell Burdick & Jackson Co., MI, U.S.A. Sulfonate CNC (S-CNC) dispersed in water (11% solid) was purchased from the University of Maine. And, Carboxylate-CNC (C-CNC) mild acid hydrolysis was used for extraction of CNC from wood pulp as explained elsewhere [10].

**Nanocomposites:** Here, we divided nanocomposite experimental results into three categories; stiff matrix ($R \leq 100$), medium matrix ($100 < R < 10^3$) and soft matrix ($R > 10^3$). We use CNC nanocomposites experiments, done in our lab, and filled gaps in results from others experiments. At the end, we showed that it works for other nanocomposites as well. For stiff matrix, we chose PMMA, polysulfone (PSf) and Poly (vinylidene fluoride) (PVdF). We used the same fabrication process (solution casting) for theses composite films as explained elsewhere [15, 16]. Briefly, CNC was dispersed in DMAc with solvent exchange method and polymers deserved in the solution (The total solution solids were 5%) to reach desired CNC/polymer ratio (different volume factions ($V_f$) and solvent was evaporated using centrifugal casting. Young’s modulus of nanocomposites films were measured as explained in details elsewhere [15, 16]. Table 4.1 and 4.2 show more details about other nanocomposites (and their Young’s modulus) that are being used to evaluate models.
Table 4.1: CNC nanocomposites properties measured from experiments and used in the models.

<table>
<thead>
<tr>
<th>Nanocomposite</th>
<th>$E_m$ (GPa)</th>
<th>$E_f$ (GPa)</th>
<th>$\rho$</th>
<th>diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA/S-CNC</td>
<td>2.3</td>
<td>105</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>PSf/S-CNC</td>
<td>1.65</td>
<td>105</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>PVdF/S-CNC</td>
<td>1.4</td>
<td>105</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>PVdF/C-CNC</td>
<td>1.4</td>
<td>105</td>
<td>12</td>
<td>20</td>
</tr>
<tr>
<td>LDPE/S-CNC [17]</td>
<td>0.385</td>
<td>105</td>
<td>84</td>
<td>20</td>
</tr>
<tr>
<td>PVdF-HFP/S-CNC [18]</td>
<td>0.6</td>
<td>105</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>PU/S-CNC [19]</td>
<td>0.041</td>
<td>105</td>
<td>13</td>
<td>20</td>
</tr>
<tr>
<td>WPU/S-CNC [20]</td>
<td>$5 \times 10^{-4}$</td>
<td>105</td>
<td>15.5</td>
<td>24</td>
</tr>
<tr>
<td>Polyether/S-CNC [21]</td>
<td>8.1 $\times 10^{-4}$</td>
<td>105</td>
<td>80</td>
<td>15</td>
</tr>
<tr>
<td>Latex/S-CNC [22]</td>
<td>$5 \times 10^{-5}$</td>
<td>140</td>
<td>67</td>
<td>10</td>
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Table 4.2: Other nanocomposites (CNT and nanoclay) properties measured from experiments and used in the models.

<table>
<thead>
<tr>
<th>Nanocomposite</th>
<th>$E_m$ (GPa)</th>
<th>$E_f$ (GPa)</th>
<th>$\rho$</th>
<th>diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR/nanoclay [23]</td>
<td>$6.4 \times 10^{-4}$</td>
<td>178</td>
<td>26</td>
<td>10</td>
</tr>
<tr>
<td>NBR/nanoclay [23]</td>
<td>$1.6 \times 10^{-3}$</td>
<td>178</td>
<td>27</td>
<td>10</td>
</tr>
<tr>
<td>CNBR/nanoclay [23]</td>
<td>$2.12 \times 10^{-3}$</td>
<td>178</td>
<td>31.5</td>
<td>10</td>
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<td>Nylon 6/nanoclay [24]</td>
<td>2.75</td>
<td>178</td>
<td>57</td>
<td>1</td>
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<tr>
<td>NBR/MWCNT [25]</td>
<td>$3.28 \times 10^{-3}$</td>
<td>180</td>
<td>29</td>
<td>20</td>
</tr>
<tr>
<td>polyimide/MWCNT [26][27]</td>
<td>2.84</td>
<td>200</td>
<td>100</td>
<td>50</td>
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</table>
4.3 Models

4.3.1 Mori-Tanaka model (MT)

Tucker and Liang 1999 [11], extensively explained the Mori-Tanaka (MT) model and other models that are essentially identical to MT (e.g., Ferrari and Chows) [11]. Briefly, MT is a model that extends the Eshelby model [28] to the case for non-dilute fibers in a composite. In the Eshelby approach, an elliptical region in a homogenous material (matrix) is replaced with another material (ellipsoid shape fiber), and they have a perfect interface. It is the same as replacing the fiber with matrix material and having an internal transformation strain ($\epsilon^T$), or the eigenstrain, inside the ellipsoid, plus an internal strain in the matrix ($\epsilon^C$) with no stress on the surface of ellipsoid. Then a uniform strain ($\epsilon^A$) is applied to homogenous material far away from fiber (see Fig. 4.3.1.1). The stress on fiber can be written in two ways:

$$\sigma_f = C_f (\epsilon^A + \epsilon^C) = C^m (\epsilon^A + \epsilon^C - \epsilon^T) \quad (4.3.1)$$

Where $C_f$ and $C^m$ are stiffness tensor of fiber and matrix. Stiffness tensor of composite (C) is found using Eq. 4.3.2. Here $A_f$ is called concentration tensor [11].

$$C = C_m + V_f (C_f - C_m) A_f \quad (4.3.2)$$

$A_f$ for Eshelby is:

$$A_f^{Eshelby} = [I + \lambda S^{m^e} (C_f - C^m)]^{-1} \quad (4.3.3)$$

Here, $S^{m^e}$ is compliance tensor of matrix and $\lambda$ is Eshelby constant and only depends
on fiber aspect ratio ($\rho_f$) and the matrix elastic constants. Eshelby is only for dilute concentrations ($< 1\%$) and not accurate for higher volume fractions. Mori-Tanaka (MT) approach can be reduced to a modification to $A_f$ tensor of Eshelby that accounts for fiber volume fractions:

$$A_f^{MT} = A_f^{Eshelby}[(1 - V_f)I + V_f A_f^{Eshelby}]^{-1} \quad (4.3.4)$$

Tucker and Liang 1999 [11], found concentration tensor ($A_f$) for other models similar to Eshelby. Self-consistent (SC) model also is similar to Eshelby (or Mori-Tanaka) that is being used for short fiber composites [29 30 31 32]. The difference is that SC assumes a fiber (or particle) is embedded in the composite [29]. In the other words, it isolates one fiber embedded in the composite (instead of one fiber in a homogenous matrix). The concentration tensor for SC ($A_f^{SC}$) can be calculated directly (with some assumptions) for spherical particles [29] and aligned continuous-fibers [30]. For short fiber composite, $\lambda^{SC}$
calculation is more difficult than $\lambda$ in Eshelby. Because, in contrast to Eshelby, which assumes that the ellipsoid fiber is embedded in an isotropic matrix, in SC fiber is embedded in a transverse isotropic composite [11]. For instance, Lin and Mura 1973, only calculated $\lambda^{SC}$ for anisotropic and transversely isotropic matrix with spherical short fibers [33]. $A^{SC}_f$ for short fibers is usually calculated by iteration using Eq. (4.3.2) and (4.3.3). Calculation starts by guessing C (stiffness matrix of composite) to calculate $A^{SC}_f$ from Eq. (4.3.3), and then, use equation (4.3.2) to calculate new C and continue iterations until C is converged. SC model has a better view (assumption) over the fiber-matrix interactions, the effective modulus is calculated numerically and it can be time-consuming.

Generally, Mori-Tanaka (or models with similar approach) gives a good estimation for traditional short fibers [11]. For nanocomposites MT estimation would be reliable as long as the interface between fiber and matrix is perfect and $R$ value ($E_f/E_m$) is less than 100 [6]. Hua and Brinson 2005, suggested to numerically calculate $A_f$ for different nanoparticles to predict the stiffness of nanocomposites (hybrid numerical-analytical) [9], but their method can be applied only if a numerical method is available for $A_f$.

4.3.2 Bounding Model

Bounding methods give an upper and a lower bound (depending upon boundary condition) for elastic properties, and guarantees that the stiffness of composite would fall between these bounds rather than exact answer for the stiffness of composite. This method was first introduced for continuous unidirectional fiber composites [12], assuming that a cylindrical isotropic continuous-fiber is embedded in an isotropic matrix, and the composite is transversely isotropic. Then the "upper" and "lower" bounds of properties can be calculated using uniform displacement and stress boundary conditions, respectively (Voigt and Reuss bounds) [11]. Hashin and Rosen 1964 [12], introduced upper and lower
bounds for anisotropic continuous-fiber embedded in an isotropic matrix with the assumption that the composite is transversely isotropic.

Hashin and Shtrikman 1962 [34], introduced stress (and strain) polarization tensor to bring bounds closer [34]. They assumed that the composite is quasi-isotropic, and a small part of the composite is replaced by a reference cube with a polarized tensor only inside the cube (see Fig. 4.3.2.1). Their calculation showed if the reference material is the softest material in the composite (which usually is the matrix), the new bound is highest lower bound; and if the reference material is the stiffest component of composite (fiber), it gives lowest upper bound. Also, using zero and infinity as reference materials gives the inverse rule of mixture and rule of mixture respectively.

This stress (strain) polarization of reference cube was a similar analogy to Eshelby model as explained above. Their original calculation was for bulk and shear modulus of spherical composites. The innovation of their method was that the stress polarization is a function of both shear and bulk modulus of both components. In the other words, the bulk modulus (and shear modulus) of a composite is a function of shear and bulk modulus of its components. In 1966, Walpole [35, 36], approximately calculated the polarization tensors for a uniform isotropic composite with arbitrary geometry (arbitrary anisotropic) and then for anisotropic reference (sphere or ellipsoid) material [35, 36]. These bounds (with the polarization tensors) are usually called Hashin-Shtrikman-Walpole (HSW) bounds and only give a good estimation for isotropic composites (the anisotropic ellipsoid case was iteratively solved by Walpole as an approximation).

Willis 1977, mixed HSW and self-consistent models explicitly for aligned elliptical short fibers (anisotropic) with circular cracks in them to find polarization tensors. But, the results were only for thermal conductivity of isotropic matrix with isotropic spherical particles. Elastic properties were not discussed due to complexity for calculation of polarization tensors [37]. Overall, HSW gives decent bounds for short fibers if they are
4.3.3 Halpin-Tsai (HT)

Halpin-Tsai (HT) model attempts to generalizes the upper bound and lower bounds and derive a simpler results \[38\]:

\[
\frac{\bar{P}}{P_m} = \frac{1 + \eta \xi V_f}{1 - \eta V_f}, \quad \eta = \frac{P_f - 1}{P_f + \xi}
\]  

Here, $\bar{P}$, $P_f$, and $P_m$ are composite, fiber and matrix properties, respectively. $\xi$ is a measure of reinforcement which depends on the geometry of inclusion (fibers) and boundary conditions. For $\xi = 0$ the HT equation gives lower bound (inverse rule of mixture), for $\xi = \infty$ gives upper bound (rule of mixture), and for any other value the equation is between these two bounds \[38\].

The Halpin-Tsai (HT) model started by rewriting Hooke’s law for a unidirectional continuous-fiber composite (see Fig. 4.3.3.1) and the stiffness (or compliance) matrix was
Figure 4.3.3.1: Halpin-Tsai figure shows that the calculation is for continuous fiber composites.

calculated using Hill’s (R. Hill 1963) notation [39]. $\xi$ is a factor that fits the model with experiments. Halpin and Tsai 1969 [38], numerically calculated $\xi$ as a function of aspect ratio ($\rho$). They assumed the composite is transversely isotropic and calculated axial and transverse elastic moduli ($E_{11}$ and $E_{22}$) and shear modulus ($G_{12}$). Their results suggested that $\xi = 2\rho$ for $E_{11}$, $\xi = 1$ for $E_{22}$, and $\xi = \sqrt{3} \log(2\rho)$ for shear modulus [38]. These calculations can only be applied for especial cases (either unidirectional continuous-fiber or isotropic short fiber composites 2D (plain stress) with low R value). For composites with high aspect ratio or high R value, HT underestimate the composite properties [11, 14], and it is close to lower bound models.

Halpin and Tsai 1969 [38], also derived the HT equation (Eq. 4.3.5) in the form of generalized Einstein’s equation (Eq. 4.3.6) for dilute rigid inclusion in an incompressible matrix ($\nu = 0.5$), which could be a decent assumption for high $R$ in nanocomposites. Generalized Einstein’s equation (for composites) first was introduced for the viscosity of a media with colloidal suspensions [40]. Imagine a particle is dispersed in a medium or matrix (the medium can be solid or liquid), and the particle property is infinite comparing
to the medium, then the properties of the composite can be written as:

\[ P^* = P[1 + \alpha_1 c + \alpha_2 c^2 + \alpha_3 c^3 + \cdots] \quad (4.3.6) \]

Here, \( P^* \) and \( P \) are properties of composite and matrix, and \( c \) is the concentration of spherical particles \( (V_f) \). These properties \( (P) \) could be, for instance, dielectric constant, viscosity, thermal conductivity or elastic modulus.

The coefficients in Eq. 4.3.6 \( (\alpha_1, \alpha_2, \alpha_3, \cdots) \), in general, are difficult to find. Comparing Eq. 4.3.6 and 4.3.7, Halpin and Tsai 1969, assumed \( \alpha_1 = (1+\xi)\eta \) and other coefficients are negligible for elastic modulus \( [38] \).

\[ \frac{\bar{P}}{P_m} = 1 + (1 + \xi)\eta V_f[1 + \eta V_f + (\eta V_f)^2 + \cdots] \quad (4.3.7) \]

**4.3.4 Guth**

Guth 1945 \( [40] \), used generalized Einstein’s equation (see Eq. 4.3.6) to predict viscosity and elastic modulus of spherical (and fiber) composites, and calculated \( \alpha_1 \) and \( \alpha_2 \) for the viscosity of fluid medium with rigid colloidal suspension \( (\eta^*) \), assuming that other coefficients are negligible:

\[ \eta^* = \eta[1 + 2.5c + 14.1c^2] \quad or \quad E^* = E_m[1 + 2.5V_f + 14.1V_f^2] \quad (4.3.8) \]

This model was validated using experimental results of viscosity. For modulus, it is assumed that the reinforcement mechanism for elastic modulus and viscosity are the same \( (i.e., \) they have the same coefficients). Equation (4.3.8) thus shows Guth prediction for Young’s modulus of composites \( (E^*) \) with spherical particles \( [40] \). For composite with
rigid fibers of different aspect ratios ($\rho$), $E^*$ is calculated using Eq. 4.3.9 [41].

$$E^* = E_m[1 + 0.67\rho V_f + 1.62\rho^2 V_f^2]$$  \hspace{1cm} (4.3.9)

Although polymers are viscoelastic materials, assuming physics of viscous flow are the same as elasticity seems unreasonable. For instance, in viscous media particles are not fixed, and have a degree of freedom (to move or rotate based on colloidal suspension) but for elasticity the assumption is that particles positions are not time dependent, but are fixed. Furthermore, Guth does not count for fiber orientation in the matrix, and assumes they are randomly oriented.

The Guth model has been widely used to predict elastic modulus of nanocomposites, but for high $R$ value usually is close to lower bound models (underestimates the properties). Modeling elastic properties of nanocomposites with high $R$ value (e.g., reinforcing elastomers with nanoparticles) using a combination of viscous and elastic models could be a more reasonable approach to predicting modulus of polymer nanocomposites.

### 4.3.5 Lewis-Nielsen

Lewis and Nielsen 1970, proposed a combination of viscosity and elasticity to predict elastic modulus of low stiffness matrix composites [42], assuming that a viscosity model can be used to calculate elastic modulus (relative modulus) under two conditions — $R \to \infty$ and composite has continuous fibers. The Lewis-Nielsen equation accounts for the maximum volumetric packing fraction of particles ($V_{f_{\text{max}}}$). For volume fractions higher than $V_{f_{\text{max}}}$, the composite is considered continuous ($V_f > V_{f_{\text{max}}}$):

$$\frac{\bar{P}}{P_m} = \frac{1 + \xi \eta V_f}{1 - \Psi(V_f)\eta V_f}$$  \hspace{1cm} (4.3.10)
where $\Psi(V_f)$ is a function that satisfies three boundary conditions to have generalized Einstein’s equation at low $V_f$:

$$
\begin{align*}
\Psi(V_f) &= 0 \quad \text{at} \quad V_f = 0 \\
\Psi(V_f) &= 1 \quad \text{at} \quad V_f = V_{f_{\text{max}}} \\
\frac{d\Psi(V_f)}{dV_f} &= 1 \quad \text{at} \quad V_f = 0
\end{align*}
$$

Lewis and Nielsen found two functions that would fulfill these conditions with good agreement with experimental results (spherical glass particles in elastomers):

$$
\begin{align*}
\Psi(V_f) &= 1 + \left(1 - \frac{V_f}{V_{f_{\text{max}}}}\right)V_f \\
\Psi(V_f) &= V_f^{-1}\left[1 - \exp\left(-\frac{V_f}{V_{f_{\text{max}}}}\right)\right]
\end{align*}
$$

Although Lewis - Nielsen (LN) model predicts more accurate modulus for composites with higher $R$ values (compared to HT and MT), the prediction is still inaccurate (close to HT) for high aspect ratio short fiber composite (predicts decent results for the modulus of high $R$, when $\rho \leq 10$) [11], because $\Psi$ was calculated for spherical particles [42]. Nielsen 1970, concluded that for other composites (with different particle shapes) $V_{f_{\text{max}}}$ needs to be calculated, and as a consequence, $\Psi(V_f)$ would be different [43].

4.3.6 Percolation

Another approach that has often been used to predict elastic modulus of nanocomposites especially with low stiffness matrices (elastomers) is percolation theory [22, 44, 45, 46]. Percolation was first introduced to model flow of a fluid in static random medium that showed the fluid would not flow if the concentration of medium was smaller than a per-
Figure 4.3.6.1: Takayanagi model which later was called percolation.

colation threshold (nonzero). The percolation threshold was based on the idea that a sufficiently connected medium was needed for conduction and it was explained by a lattice model [47]. In brief, the model predicts that below the threshold there is no conduction and above the threshold point, the conduction increases drastically. The threshold depends on the geometry of medium particles and flow properties of the fluid [48]. In polymer composites, percolation was used to predict the electrical conductivity of a composite with conductive particles (e.g., carbon nanotube) embedded in a non-conductive matrix [49].

Percolation was also used to model elastic properties of polymer composites based on work by Takayangi and Ouali et.al. [50] [51]. Figure 4.3.6.1 shows a schematic picture of a series/parallel model. Assume the white area is the crystalline part (stiffer or fiber in composites) and the black area is amorphous part (lower stiffness or matrix in composites). It is possible to shift all black parts to the left corner based on equivalent area (it is a 2D model in which area and volume fractions are the same (Fig.4.3.6.1(a)). Now this semicrystalline polymer (or composite) can be divided in two ways. In Fig. 4.3.6.1(b) both crystalline and amorphous parts have the same strain (strain boundary
condition which gives a parallel upper bound) and in Fig. 4.3.6.1(c) stress is the same in both components (traction boundary conditions and a series lower bound). Takayanagi predict viscoelastic properties of semicrystalline polymers using this series/parallel model (and later was called percolation):

\[ E^* = \left[ \frac{\varphi}{(1 - \lambda)E_f + \lambda E_m} + \frac{(1 - \varphi)}{E_m} \right]^{-1} \quad \text{(4.3.11)} \]

Here \( E^* \) is the composite modulus. The increased modulus depends on volume fraction of fiber, \( V_f \), and aspect ratio of fibers \( \rho \). As \( V_f (= 1 - \lambda \varphi) \) and \( \rho (\propto (1 - \lambda)) \) increase, the chance of percolation increases. Takayanagi used experimental results (polyvinyl chloride (PVC) as crystalline part and nitrile-butadiene rubber (NBR) for low stiffness part) and calculated \( E^* \) as function of \( V_f \) with assumption that low stiffness part (matrix) is spherical and dispersed in fibers. This model is based on continuous-fiber model and assumes that the fiber would not reinforce the polymer if it is not end to end (continuous), which is in contrast to short fiber composite experiments. Ouali et.al. 1991, attempted to experimentally calculate percolation threshold for polymer composites and later aspect ratio (\( \rho \)) was included in the model [22, 51]:

\[ E_c = \frac{(1 - 2\psi + \psi V_f)E_f E_m + (1 - V_f)\psi E_f^2}{(1 - V_f)E_f + (V_f - \psi)E_m} \quad \text{(4.3.12)} \]

where

\[ \psi = \begin{cases} V_f (\frac{V_f - X_c}{1 - X_c})^{0.4} & \text{if } V_f \geq X_c = \frac{0.7}{\rho} \\ 0 & \text{if } V_f < X_c \end{cases} \]

Figure 4.3.6.2(a) shows a schematic picture of percolation threshold of fibers in nanocomposite materials. The problem with this assumption is that the model ignores random distribution of fibers in matrix. Also, another question that rises about this model is that, if
fibers are touching each other, is there a bond between them or not? If fibers are bonded, then it would be fiber agglomeration (and they should be seen with naked eyes or light microscopes, because the size of agglomerated fibers is from one end to the other end of composites), and aspect ratio of fibers is changed. If they are not bonded, the touching point is a void and will decrease the stiffness of nanocomposite.

Nairn and Shir Mohammadi 2015 [6], explained an analogous approach to percolation for short fiber composites in which fibers do not necessary touch each other, rather there might be a path between two ends of composites enriched in fibers \((V_f)\) is locally higher along that path) and the chance of this local \(V_f\) increase depends on volume fraction of composite and aspect ratio of fibers (see Fig. 4.3.6.2(b)).

Qiao and Brinson 2009 [8], suggested that addition of nanoparticles, could lead to formation of an interphase layer between matrix and fibers, and if the interphase volume gets large enough, the ”interphase” percolates and the stiffness of nanocomposite increases drastically (see Fig. 4.3.6.2(c)). Qiao and Brinson used FEA (numerical model) to show this increase and concluded that the interphase volume needs to be 40-80% of composite for aligned composites to percolate [8] (and lower for randomly oriented). A potential problem with this analysis is that even if scaling arguments show that increased interphase in nanocomposites can promote a percolation path, it is unclear why the properties of the interphase would be substantially different then the bulk matrix. A small difference is easy to understand (but could just are likely reduce the interphase stiffness rather then increase it), but the substantial difference needed for that path to cause dramatic reinforcement seems unlikely. Overall, the percolation threshold theory is vague about the mechanism of reinforcement in short fiber nanocomposites and is not reliable for prediction of elastic properties.
4.3.7 Shear-lag-capped (SLC)

Shear-Lag (SL) is historically the first analytical model for short fiber composites [52] and the only model that can account for imperfect interface (interphase) [53, 54, 55]. In axisymmetric shear lag models, the "unit cell" of a composite consists of a single cylinder fiber embedded in a concentric cylinder of matrix. The original SL did not count for stress at the ends of fibers (assuming instead that stress (σ) is zero at fiber ends) [53, 54, 55, 56] which was inaccurate. Nairn and Shir Mohammadi 2015 [6] derived a new shear lag model (shear-lag capped model (SLC)) where fiber is completely encapsulated by matrix and covers fiber’s ends (top and bottom of fibers), the fiber ends carry load, and the assumed thickness (distance from fiber surface to edge) is the same on the sides and ends of each fiber (δ). (see Fig. 4.3.7.1). Briefly, SLC has two interface parameters: $r_f D_t$ and $r_f D_n$ where $D_f$ and $D_t$ are interface stiffnesses for tangential and normal sliding and $r_f$ is fiber radius. When $D_t = 0$, the interface is debonded, when $D_t = \infty$ is perfect
interface, and all other values of $D_i$ model an imperfect interface. The model predicts the axial axial modulus to be:

$$\frac{E_2}{E_{EC}} = 1 + \left( \frac{E_f}{E_m} - 1 \right) (V_1 - V_f) + \frac{E_f V_f}{E_m V_m} \Lambda(\rho) \quad (4.3.13)$$

where $V_i$ is volume fraction and $E_i$ is modulus (subscripts $f$ and $m$ refer to fiber and matrix); $V_1 = r_f^2/r_m^2$ is volume fraction of fiber ignoring the end caps and $E_2 = E_f V_1 + E_m(1 - V_1)$. The key function of aspect ratio ($\rho$) was derived to be:

$$\Lambda(\rho) = \frac{V_m}{V_2} \frac{E_2}{E_f} \frac{\tanh(\beta_1^* \rho)}{\beta_1^*} + \left( 1 + \left( 1 - \frac{E_2}{E_f} \right)^2 \frac{\tanh(\beta_2^* \rho)}{\beta_1^*} \frac{\tanh(\beta_2 \rho)}{\beta_2} \right) \frac{\tanh(\beta_2 \rho)}{\beta_2} \quad (4.3.14)$$

where $\beta_1^* = (V_1 - V_f) \beta_1/(2V_f)$, $\eta = E_m V_2/(r_f D_n)$,

$$\beta_1^2 = -\frac{4G_m V_2}{E_m (V_2 + \ln V_1)} \quad \text{and} \quad \beta_2^2 = \frac{4E_2}{E_f E_m} \frac{V_2}{2G_f} - \frac{1}{E_m} \left( \frac{V_2}{2} + 1 + \ln V_1 \right) + \frac{2V_2}{r_f D_n} \quad (4.3.15)$$

Here $\beta_1$ and $\beta_2$ are two optimal shear lag parameters including imperfect interfaces [53, 54].

Nairn and Shir Mohammadi 2015 [6] used Monte Carlo finite element analysis (FEA) with fixed displacement boundary condition (BVE) to predict a rigorous upper bound for the stiffness of nanocomposites. Their results showed that SLC can predict similar results to finite element analysis (FEA) including imperfect interface between fiber and matrix but is very accurate only for $R < 100$ [6, 15], and the model becomes a lower-bound model when $R$ gets larger. Furthermore, Shir Mohammadi and Nairn (2016 hopefully) [14], and Shir Mohammadi et.al. [15] introduce a correction term to model composite properties when $R > 100$. The proposed axial modulus is
\[ E^* = \phi_L E_{EC} + (1 - \phi_L) E_{UB} \quad (0 < \phi_L < 1) \]  

(4.3.16)

where

\[ E_{UB} = \eta_f E_f V_f + E_m V_m \]  

(4.3.17)

Here \( E_{UB} \) is an “upper bound” modulus derived using fiber effectiveness methods advocated in several text books \[57\], where \( \eta_f \) is found by comparing average stress in the fiber to the stress the fiber would have in a continuous fiber composite:

\[ \eta_f = \frac{1}{l_f \sigma_\infty} \int_{-l_f/2}^{l_f/2} \sigma_f(z) \, dz \]  

(4.3.18)

where \( l_f \) is fiber length, \( \sigma_\infty \) is stress that would be in an infinitely long fiber, and \( \sigma_f(z) \) is average stress in the fiber cross section at position \( z \). Evaluating this integral using the end-capped shear lag stress (with imperfect interfaces) rather than the simplistic shear lag \([57]\) gives

\[ \eta_f = 1 - \frac{1 + \left(1 - \frac{E_f}{E_2}\right) \frac{\tanh(\beta_1 \rho)}{\beta_1 \eta} \tanh(\beta_2 \rho)}{1 + \frac{\tanh(\beta_1 \rho)}{\beta_1 \eta} + \frac{E_2}{\eta E_f} \frac{\tanh(\beta_2 \rho)}{\beta_2}} \]  

(4.3.19)

and

\[ \frac{E_{UB}}{E_c} = 1 - \frac{E_f V_f}{E_c} \frac{1 + \left(1 - \frac{E_f}{E_2}\right) \frac{\tanh(\beta_1 \rho)}{\beta_1 \eta} \tanh(\beta_2 \rho)}{1 + \frac{\tanh(\beta_1 \rho)}{\beta_1 \eta} + \frac{E_2}{\eta E_f} \frac{\tanh(\beta_2 \rho)}{\beta_2}} \]  

(4.3.20)

where \( E_c = E_f V_f + E_m V_m \).

The bounding factor \( \phi_L \) is found for wide range of nanocomposites (different \( R \) and \( \rho \) values) using upper bound Monte Carlo FEA (or BVE) for wide range of nanocomposites (different \( R \) and \( \rho \) values) \[14\]. In a simple words, \( \phi_L \) could be explained as \textit{in situ} efficiency \( \eta_f^{SLC} \) of fibers that depends upon \( R \) value and \( \rho \) of fibers in the composite.

Details about \( \phi_L \) calculation and ”solution map” can be found elsewhere \[14, 15\]. Here, we compare bounded SLC, and other mentioned analytical models with experi-
Figure 4.3.7.1: Shear-Lag model assuming $\sigma = 0$ at the end of fiber.

4.4 Discussion

4.4.1 High stiffness polymers ($R < 100$)

Figure 4.4.1.1 compares experimental results of young’s modulus ($E_c$) vs. volume fraction of CNC ($V_f$) for glassy polymer ($R < 100$) nanocomposites comparing with different analytical models. The percolation model does not fit experiment results. As explained before, percolation theory is not based on mechanism of reinforcement for short fiber composites. It was used to fit data for storage modulus of nanocomposites, but it is not a reliable design model.

Other models (SLC, HT and MT) are almost the same if we assume that we have perfect interface between the matrix and fibers. For instance, using any model that assumes perfect interface between fiber and matrix would predict to have almost the same modulus in PVdF and PSf with addition of CNC (because pure PSf and PVdF have almost the same young’s modulus). But, comparing the experiments, these two nanocomposites shows different results. The Young’s modulus of PVdF increases more comparing
to PSf, with addition of CNC. The only explanation for this difference is the compatibility of polymer with CNC at the interface. In the other word, CNC has better interface with PVdF than PSf to transfer the load from matrix to fiber and that causes a greater increase in stiffness. Using the SLC model with imperfect interface shows this difference (the interface is almost an order of magnitude stiffer between CNC/PVdF compared to CNC/PSf).

These comparisons between polymers were done using sulfonate CNC (S-CNC). Comparing increases in the Young’s modulus of PVdF with addition of S-CNC to carboxylate CNC (C-CNC) (see Fig. 4.4.1.1(c)), shows that C-CNC/PVdF has lower modulus than S-CNC/PVdF. This can be explained by the difference between CNC surface modifications. S-CNC has better bonding with PVdF compared to C-CNC. So, interfacial properties play an important rule in reinforcement of high stiffness (glassy) polymers and small changes in interface properties causes different results in modulus of nanocomposites. For these nanocomposites ($R < 100$), short fiber models with perfect interface predict almost the same upper bound with addition of nanoparticles (maximum modulus that can ideally be achieved). The advantage of the SLC model is that it accounts for imperfect interface, which can used to fit experiments. Similar calculations are not possible with other models.

4.4.2 Effect of aspect ratio ($\rho$) and R

For a medium stiffness matrix ($100 < R < 1000$) we chose PVdF-HFP and LDPE results reinforced with CNC [17][18]. Figure 4.4.2.1 shows experimental results and different analytical models for these two polymer nanocomposites. The difference between these two nanocomposites is the aspect ratio of the CNC fibers. These two types of fibers extracted with the same process (acid hydrolysis using sulfuric acid) from different sources (wood
Figure 4.4.1.1: Comparing experimental results of glassy polymer nanocomposites with analytical models. PMMA (a), PSf (b) and PVdF (c) with to different surface modification of CNC, sulfonate (○) and carboxylate (□).
pulp [18] and tunicate CNC [17]). So, we assumed the surface modification and stiffness along the fiber for both CNCs are the same, and the only difference is aspect ratio ($\rho$).

In LDPE/CNC (Fig. 4.4.2.1a and c), the average aspect ratio was 84, and in PVdF-HFP/CNC (Fig. 4.4.2.1b and c) it was 18. As the experiments show, the stiffness of LDPE increases more than PVdF-HFP with addition of CNC (at the same amount in both nanocomposite) because fibers have higher aspect ratio. For both nanocomposites, the HT model underestimates the modulus of nanocomposites especially for higher aspect ratio (in LDPE/CNC nanocomposites). SLC and MT are in good agreement with experiments in PVdF-HFP/CNC (for low aspect ratio) but for high aspect ratio fibers MT overestimate the Young’s modulus. Using the solution map for SLC with imperfect interface [14] (solid lines in Fig. 4.4.2.1) shows PVdF-HFP has better interface ($D_t = D_n = 0.5$ GPa) with CNC than LDPE ($D_t = D_n = 0.1$ GPa), but the difference in aspect ratio is more dominant here. Details about the solution map can be found elsewhere [14].

4.4.3 Soft matrices ($R > 1000$)

For rubbery polymers we chose four different nanocomposites from the literature (see Fig. 4.4.3.1) [19, 20, 21, 22]. They all had CNC fibers with different aspect ratios (see Table 4.1). For these nanocomposites with $R > 1000$, we compared the Guth model with experiments, as well (which is often used to compare rubbery nanocomposites in other work).

In all experiments, the percolation model poorly predicts the elastic modulus of nanocomposites because, as was mentioned before, the assumption for this model is based on continuous-fiber composites and it is not reliable for short fiber composite predictions. The HT, MT and Guth models all underestimate the modulus of nanocomposites and experiments are above predictions (i.e., the predictions are close to lower bounds in these
Figure 4.4.2.1: Comparing experimental results of medium stiffness (100 < R < 1000) polymer nanocomposites with analytical models. LDPE (a), PVdF-HFP (b) and log scale plots (c) to compare polymers, PVdF-HFP (○) and LDPE (○).
models). In contrast, the upper bound SLC model (using φL = 0.93 based on solution map as was explained elsewhere [14]), shows predictions that are, as expected, above the (experiments do not exceed predictions based on good upper bound continuum mechanics). The dotted lines in Fig. 4.4.3.1 shows SLC first using and imperfect interface. Changing the interface properties (Dt and Dn) in the SLC makes the model fit the experiment for lower volume fraction (see Fig. 4.4.3.1(c)). But looking at experimental data, and comparing with SLC upper and lower bound curves, suggests that with increasing Vf, experiments go through a transformation from lower bound to being closer to upper bound (see Fig. 4.4.3.1(b, c and d). These experiments suggest that the interface (Dt and Dn) could be a function of volume fraction and aspect ratio (ρ). In other words, D might change with ρ and Vf. This change in D value can be explained by changing the molecular structure of matrix with addition of nanoparticles.

Analytical models usually assume no change in structure of matrix and nanoparticles (assume matrix and nano inclusion do not interact at a molecular level). Even, SLC model assumes formation of an interface between matrix with no change in the structure of composite materials. But in real life, some literature reported changes in the structure of polymer matrix with addition of nanoparticles [7, 16, 58, 59, 60]. So, a change in D value for different ρ and Vf could be explained by structural changes in the nanocomposites.

One might ask — why does this transformation only happen in low modulus nanocomposites (with high R value)? This was explained by Nairn and Shir Mohammadi 2015 [6]. All composites can be modeled by a bounding method (upper and lower bounds), which predicts the most optimistic and pessimistic moduli of composites. These two bounds are close when the R value is small and experiments match the bounds (experiments are between the two close bounds). As R increases, the bounds get farther apart and the experiments still fall between the bounds. Furthermore, at higher Vf, the chance of having a locally increased volume faction increases (see Fig. 4.3.6.2), which is similar analogy
Figure 4.4.3.1: Comparing experimental results of low stiffness ($R > 1000$) polymer nanocomposites with analytical models. PU (a), WPU (b), Polyether with high aspect ratio CNC (c) and latex with high aspect ratio CNC (d).
to percolation without fibers necessarily touching each other [6], is increased.

4.4.4 In-situ fiber efficiency ($\eta_f^*$)

In-situ efficiency of fibers ($\eta_f^*$) is similar to fiber effectiveness ($\eta_f$), which shows how well the fibers are reinforcing the composite. 0 means no reinforcement and 1 is the maximum reinforcement (rule of mixtures) in an aligned continuous fiber composite. For randomly oriented composites this factor drops to $\frac{1}{\pi}$ (the maximum theoretical reinforcement). All models can be rewritten based on in-situ fiber efficiency (similar to Eq. 4.3.17). Plotting composite modulus based on in-situ fiber efficiency is an easy way to compare experiments with models.

Here, we also divided short fiber nanocomposites into three categories based on $R$ value ($\frac{E_f}{E_m}$). Figure 4.4.4.1(a) shows $\eta_f$ vs. $V_f$ for PSf and PVdF nanocomposites. Solid lines (PSf) and dotted lines (PVdF) are results of different models (SLC (black), MT (green) and HT (blue) with a perfect interface. All models predict almost the same fiber efficiency (around 0.2) for PSf and PVdF (high stiffness polymers) but experiments show an obvious difference. In PVdF, $\eta_f$ is around 0.1 (for S-CNC incorporated with PVdF) while it is around 0.05 for PSf. On the other hand, using the SLC model with an imperfect interface can predict the same efficiency as experiments (dashed line are SLC fits using an imperfect interface). Figure 4.4.4.1(b) shows that LDPE nanocomposites with high aspect ratio CNC have higher fiber efficiency (around 0.2) than PVdF-HFP nanocomposite with CNC fibers have aspect ratio of 18 (0.07 to 0.1). Also, it is clear that HT underestimates, and MT overestimates the in situ fiber efficiency as $\rho$ increases.

For rubbery nanocomposites, the results are different. In experimental results, there is a transformation in fiber efficiency from 0 to a constant value, as volume fraction of fibers increases (transformation from lower bound to upper). This transformation is faster
Figure 4.4.4.1: Fiber efficiency in nanocomposites. For $R < 100$ comparing PVdF ($\diamond$) and PSf ($\circ$) in (a). For $100 < R < 1000$ comparing LDPE ($\diamond$) and PVdF-HFP ($\circ$) in (b). For $R > 1000$ comparing latex ($\diamond$) and WPU ($\circ$) in (c). Blue line are HT, green MT and black SLC upper bound. dotted lines.

for fibers with higher aspect ratio ($\propto \rho$). HT and MT predictions are close to lower bound for fiber efficiency ($\eta_f \sim 0$). Interestingly, Guth model shows the same shape for $\eta_f^\ast$ vs. $V_f$ and increases with volume fraction. Also, this transformation is faster for high aspect ratio fibers. But, the results are more than an order of magnitude lower than experiments. In Guth model, $\eta_f^\ast$ gets close to zero for low stiffness polymers ($\eta_f^\ast \propto \frac{1}{R}, \rho^2$ and $V_f$). Although Guth model predicts the right shape for $\eta_f^\ast$ function (compared with experiments), it underestimates the modulus and is close to lower bound modulus.

An upper bound SLC model predicts the maximum achievable $\eta_f^\ast$ for high $R$ nanocomposites. In experiments $\eta_f^\ast$ starts from lower bound and gets close to SLC results at high volume fraction. It worth to mentioning again that in Fig. 4.4.4.1 the fiber efficiency of the SLC model was plotted by assuming that the interface is perfect. For imperfect interface efficiency, the predictions are lower lower ($\eta_{f,\text{max}}^\ast \sim 0.02$ for high $R$ nanocomposite with perfect interface).
4.4.5 Other nanocomposites

The previous examples compare CNC nanocomposite results to different models prediction. Next, we compared \( \eta_f \) of experimental results from two other type of nanoparticles that are being used to reinforce polymers (nanoclay \([23, 24]\) and carbon nanotube (CNT) \([25, 26, 27]\)) using the SLC model. Table 4.2 gives properties of nanocomposites that were used to generate the plots in figure 4.4.5.1. SLC predicts (see Fig. 4.4.5.1(a)) in Nylon/nanoclay composites with high aspect ratio and aligned fibers (\( R < 10^{6} \), \( \rho \) is 57 and they are aligned), the theoretical in situ \( \eta_f \) (if fiber and matrix have perfect interface bond) is 0.8 and experimental result is around 0.6. This smaller value can be fit to SLC model with an imperfect interface or \( \eta_f = 0.6 \) when \( D_t = D_n = 33 \text{MPa} \).

For a rubbery matrix (SBR(\( \diamond \)), NBR(\( \diamond \)) and CNBR (\( \triangle \))) the results are between upper and lower bounds (and closer to lower bound). The dashed lines in Fig. 4.4.5.1 are SLC with imperfect interface fitting with experiments. Interestingly, the SLC upper bound with perfect interface predicts \( \eta_{f_{max}} \sim 0.02 \) for all of rubbery nanocomposites (\( R > 10^4 \))
regardless of aspect ratio (composites with higher aspect ratio reach $\eta_f = 0.02$ at lower volume fraction but $\eta_{f_{max}}$ is the same).

Finally, Fig. ??(b) shows $\eta_f vs. V_f$ for CNT nanocomposites. The results are similar to other nanoparticles. For glassy polymers (with randomly oriented fibers) the $\eta_{f_{max}}$ is 0.2 if interface was perfect interface (solid lines), but experiments are around 0.1 (here SLC fits experiments when $D_t = D_n = 0.25 \text{ MPa}$). For rubbery nanocomposites $\eta_{f_{max}}$ is 0.02 (if interface was perfect), but experiments are close to lower bound (the experiments show low interface properties between NBR and CNT).

4.5 Conclusion

In this chapter we compared different analytical models with experiments to find out which model can be used to predict the stiffness of nanocomposites. Among all models that were discussed, the shear-lag-capped (SLC) model with solution map (considering both interface and $\phi_L$) showed better results, for wide range of nanocomposites, than other models. Although, interface properties ($D_t$ and $D_n$) play an important rule in the modulus of nanocomposites, experimental measurement of interface properties on the nanoscale is the "Achilles’ heel" for stiffness prediction of these composites [14]. But, ($D_t$ & $D_n$) can be used as a measurement for interface properties, by comparing with experiments (macro scale), and once it is known between each matrix and nanoparticle, it can used to predict modulus of composite for different volume fractions ($V_f$).

As $R$ (stiffness mismatch) gets larger in nanocomposites, the stiffness predictions get more complicated and more variables are involved (the interface, $\phi_L$, $V_f$, and the relation between these variables). To have more accurate prediction, the effect of $V_f$ and $\rho$ on $\phi_L$, $D_t$ and $D_n$ needs to be considered, which makes the calculation more complex. So, using $\phi_L$ with a solution map [14], which guarantees that the experiments would not exceed the
prediction, and offers a rigorous upper bound that can be used to predict the possibility of achieving desired elastic properties in nanocomposites. Furthermore, the experiments indicated that for rubbery nanocomposites (high $R$ value), the stiffness of nanocomposites gets close to upper bound SLC at higher $V_f$ and $\rho$ if the interface is perfect. But, for imperfect interface the results are close to lower bound, which shows the importance of the interface in the mechanical properties of nanocomposites.

Fiber efficiency is a simple way to predict stiffness of nanocomposites. We showed for rubbery nanocomposites ($R > 10^4$), with randomly oriented fibers, the maximum fiber efficiency ($\eta_{f_{max}}^* = 0.02$) is good approximation for maximum theoretical stiffness based on continuum mechanics, and $\eta_{f_{max}}^*$ increases up to $\sim 0.3$ for glassy nanocomposite ($R < 100$), with perfect interface. But, usually the achievable $\eta_{f_{max}}^*$, in experiments, is lower because of imperfect interfaces.

In our opinion, using $\eta_{f_{max}}^*$ based on what we explained here is an easy way to compare experiment with theories based on continuum mechanics, and the experiment should not exceed the theoretical predictions, and if experiments exceed those prediction, new perhaps a mechanics would needed for modeling the stiffness of nanocomposites.

Bibliography


Science is the acceptance of what works and the rejection of what does not. That needs more courage than we might think.

Jacob Bronowski

The fracture toughness of polymer cellulose nanocomposites using the essential work of fracture method

This work reinforced both a glassy polymer (high stiffness matrix) and a rubbery polymer (low stiffness matrix) with cellulose nanocrystals (CNC) derived from natural sources. CNC addition always increased stiffness while it increased toughness for a rubbery polymer and caused no loss in toughness for a glassy polymer. These results contradict many
claims that when stiffness increases, the toughness decreases. We show that these claims depend on how toughness is measured. Our results were based on toughness measured using the essential work of fracture method (EWFM). In contrast, toughness determined from area under the stress-strain curve shows a significant decrease, but that method may be a poor measure of toughness. Property enhancements usually require a good fiber/matrix interface. We used modeling of stiffness properties to confirm CNC has a good interface with the studied polymer matrices.

5.1 Introduction

Nanofillers are often used to increase polymer mechanical properties, such as modulus, yield strength, ultimate strength [1, 2], ductility [3] and toughness [4]. Measuring nanocomposite toughness, however, can be a challenge. Some studies use total work of fracture ($W_f$ defined as area under the stress-strain curve) to measure “toughness” [3, 5, 6, 7]. Our view is that $W_f$ is not a material property and therefore not an ideal indicator of toughness. Instead, toughness should be associated with the amount of energy required to extend an existing crack by a unit amount of area [8].

Crack extension toughness can be measured by critical stress intensity factor, $K_c$, or by energy required to propagate a crack, $G_c$. These experiments are commonly done in opening or mode I because mode I $K_c$ and $G_c$ are usually the lowest toughnesses and therefore a critical test in nanocomposites for role of fillers on toughness properties. Measurement of mode I $K_c$ requires specialized specimens while $G_c$ can be measured on any specimen by directly measuring energy released as a function of crack growth
If either one can be measured, the other can be calculated by the relations:

\[
K_c = \sqrt{\frac{G_c E}{1 - \nu^2}} \quad \text{(if plane strain)} \\
K_c = \sqrt{G_c E} \quad \text{(if plane stress)}
\]  

where \(E\) is Young’s modulus in the applied stress direction and \(\nu\) is Poisson’s ratio. Under plane strain conditions \(K_c\) and \(G_c\) are usually called \(K_{Ic}\) and \(G_{Ic}\) and are material properties. In plane stress conditions, \(K_c\) and \(G_c\) are still useful, but may depend on specimen thickness.

The fracture toughness of brittle polymer nanocomposites (e.g., epoxy/carbon nanotube) has been measured using both impact tests (a \(K_c\) method) \([13]\) and crack propagation (a \(G_c\) method) \([14]\). These tests show that nanofiller addition increases fracture toughness provided the interface between fibers and the matrix is good \([15]\) and the nanofillers are well dispersed \([13]\). The experiments here used thin nanocomposite films, which is a common form for making nanocomposites. Unfortunately, typical impact or crack propagation tests do not work for thin nanocomposite films, especially films derived using ductile polymers. Impact tests do not work for films and it can be difficult to objectively record crack propagation as well. Some alternate methods are needed for thin films.

Because work of fracture (\(W_f\)) experiments are easy and avoid the need to monitor crack propagation, it is tempting to resort to such tests. In brief, \(W_f\) is defined as total work per unit specimen area to break an unnotched specimen. It is found from area under the stress-strain curve:

\[
W_f = \frac{1}{W_t} \int F \, dx = L \int \sigma \, d\varepsilon
\]  

where \(W, t,\) and \(L\) are specimen width, thickness, and length, \(F\) is applied force, \(x\) is
displacement, $\sigma$ is applied stress, and $\varepsilon$ is strain. Because final failure must be associated with crack initiation and propagation across the specimen, one could speculate that $W_f$ is an average of the crack propagation fracture toughness for crack growth from zero to $W$ or

$$W_f = \frac{1}{W} \int_0^W G_c \, dx = G_c$$  \hspace{1cm} (5.1.4)$$

and equality of $W_f$ with $G_c$ assumes $G_c$ is constant. Unfortunately, many influences, such as crack initiation, edge effects, and energies not associated with crack propagation, cause $W_f$ to only be crudely related to $G_c$. When $W_f$ was used to characterize nanocellulose reinforced nanocomposites, the general trend was that stiffness increases but $W_f$ decreases as filler content increases [6, 16, 17, 18]. As a result, a consensus has emerged that nanofiller addition decreases the toughness of polymers [6, 19]. This consensus derived from $W_f$ experiments may be misleading and might change by switching to improved methods for measuring toughness.

For ductile polymers and films, an alternate fracture method, known as the essential work of fracture method (EWFM), has been advocated [20, 21, 22, 23, 24]. In brief, the EWFM measures specific work of fracture (total work of fracture per unit ligament area denoted here using lower case $w_f$) for a series of deeply, double-edge notched specimens tested in tension (Fig. 5.1.0.1). The total specific work of fracture for a given ligament length, $\ell$, is partitioned into plastic work per unit volume, $w_p$, which is confined to a plastic zone in the ligament zone (of length $\ell$), and an essential work of fracture per unit area, $w_e$, associated with crack propagation. The specific work of fracture becomes

$$w_f = w_e + \beta w_p \ell \quad \text{where} \quad w_f = \frac{1}{\ell t} \int F \, dx$$  \hspace{1cm} (5.1.5)$$

and $\beta$ is a factor describing the plastic zone shape (e.g., elliptical, circular, etc.) [22].
Figure 5.1.0.1: Deeply, double-edged, notched specimens (DDENT) tested in tension for EWFM experiments.

The experiments are to measure $w_f$ as a function of $\ell$. These results are typically linear with slope equal to $\beta w_p$ and intercept equal to $w_e$. Both these properties provide useful material properties (although they may depend on thickness [20]). The slope is related to ductility while the intercept characterizes the plane stress fracture toughness of the film or measures $G_c$. The EWFM combines the ease of work of fracture experiments (except it needs multiple specimens) with a fracture mechanics result for toughness ($w_e$). The method avoids initiation effects (by cutting notches) and edge effects (by using deep notches). It avoids the need to measure crack growth in ductile materials by using multiple specimens with different ligament lengths (the ligament length becomes total amount of crack propagation for each specimen). Importantly, the slope and intercept from EWFM separates plastic energy dissipation not associated with crack growth ($\beta w_p$) from inherent toughness or energy required to propagate a crack ($w_e$). This separation contrasts with $W_f$ experiments where these two effects are combined with unknown proportions. More details about the EWFM can be found elsewhere [8, 20, 21, 22, 23, 24].

We studied reinforcement of two different polymers with cellulose nanocrystals (CNC)
— poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) and polysulfone (PSF). Experiments show that PVdF-HFP and PSF both are compatible with CNC and addition of CNC significantly increased their stiffness [25, 26]. For toughness properties, we compared traditional \( W_f \) test methods to the EWFM. Although \( W_f \) declined significantly with added CNC, the essential work of fracture, \( w_e \), which we claim is a more rigorous measure of toughness, showed the toughness increased for PVdF-HFP and remained about the same for PSF. For both polymers, the ductility decreased and that decrease was reflected in decreased \( \beta w_p \). Additional studies used modeling to quantify interfacial properties and reanalyzed fracture data to evaluate the role of thickness when interpreting EWFM experiments.

5.2 Materials and methods

5.2.1 Materials

Sulfonate CNC (S-CNC) dispersed in water (11% solids) was purchased from the University of Maine. Dimethylacetamide (DMAc) was used as the organic solvent and it was purchased from Honeywell Burdick & Jackson Co., MI, U.S.A. The rubbery polymer, PVdF-HFP, with molecular weight of 400,000 D and density of 1.78 g/cm\(^3\) was purchased from Aldrich Chemical Co. The glassy polymer, polysulfone (PSF) with a molecular weight of 35,000 D and density of 1.24 g/cm\(^3\), was donated by Solvay Advanced Polymers (Alpharetta, GA).
5.2.2 Nanocomposite Fabrication

DMAc was added to a CNC/water solution to reach 4% CNC in DMAc (note this % content and all others in this paper are percent contents by weight). A Rotovapor (Büchi RE111, Switzerland) was used to completely evaporate water from the solution (PSF and PVdF-HFP do not dissolve in water). PVdF-HFP was dissolved in DMAc and was mixed with the dispersed CNC in DMAc to reach the desired CNC weight content in the PVdF-HFP composite and stirred for 0.5 hr at 85°C to yield a uniform solution. The total solution solids were ~5%. The same procedure was used for the PSF composites.

Centrifugal casting was used to cast films in order to reduce the trapped solvent and to get uniform thickness. In centrifugal casting, a solution is poured into a metal beaker that is attached to a motor. Then the beaker is partially sealed with a center-hole cap to contain the liquid, but allow solvent evaporation. The beaker is rotated at 1800 rpm and films are cast on the beaker wall. A heat gun is applied to the exterior of the metal beaker to control the temperature. All films were cast at 70° to 80°C.

5.2.3 Mechanical Testing

All samples were cut to 12.7 mm width and 40 mm length. The thickness of the cast films varied within and between films. We therefore measured each film’s thickness using an optical microscope (Nikon Eclipse E400) and it ranged from 20 to 80 µm. All samples were tested at room temperature using an Instron 4301 with a 100 N load cell capacity and the gage length was 20 mm. The crosshead speed was set to 1 mm/min for PVdF-HFP films. But for PSF films, due to their glassy nature, a 0.5 mm/min rate was chosen in order to reach the plastic region prior to failure. Stress-strain curves were calculated by dividing the force by the initial cross sectional area and displacement by the initial gage
length. Young’s modulus was calculated from initial slope of the stress-strain curves (up to about 0.1% strain). Offset yield stress ($\sigma_Y$) was determined by finding the intersection of a line having the initial slope of the stress-strain curve but offset by 1% strain from that curve.

### 5.2.4 Essential Work of Fracture Experiments

EWFM experiments used DDENT specimens (Fig. 5.1.0.1). Mirrored notches were cut at the centerline of the samples using a razor blade. The notch depths were varied such that the remaining ligament lengths ($\ell$) varied from 0.5 to 3.5 mm. Because our maximum thickness was $t = 80 \mu\text{m}$ and specimens widths were $W = 12.7 \text{ mm}$, all specimens were confined to the recommended range of $3t < \ell < W/3$ for measuring plane stress essential work of fracture [22]. Samples were loaded in tension and stress-strain curves were measured up to failure. Afterwards, the specific work of fracture ($w_f$) was plotted as a function of ligament length ($\ell$). Ductility was measured from the slope and essential work of fracture was calculated by extrapolating the curve to $\ell = 0$.

### 5.3 Results and Discussion

#### 5.3.1 Tensile Tests on Unnotched Specimens

Figure 5.3.1.1 (top) shows the mechanical testing results for unnotched films of both pure PVdF-HFP polymer and of PVdF-HFP/15% CNC nanocomposites. The yield strength, $\sigma_Y$, of PVdF-HFP with the addition of 15% CNC increased $\sim 2$ times, the maximum strength, $\sigma_{UTS}$, increased $\sim 30\%$, and the modulus increased $\sim 3$ times. Figure 5.3.1.1 (bottom) shows that these same properties also increased from PSF to PSF/15% CNC.
nanocomposites — $\sigma_Y$ and $\sigma_{UTS}$ increased slightly (although not a significant increase) while the modulus increased 80%. But most PSF/15% CNC films broke before 1% deformation meaning we could not measure yield strength (because the stress strain curve did not reach the 1% offset line). For these films yield strength was assumed the same as $\sigma_{UTS}$.

These increases all suggested both PVdF-HFP and PSF are compatible with added CNC and the fibers were well dispersed. Visual inspection of the films supported this claim. The increases, especially in ultimate strengths, also suggest that the CNCs did not introduce any flaws into the polymer (point of weakness for failure). Nevertheless, the total fracture energy, $W_f$, for PVdF-HFP films decreased 85% with the addition of 15% CNC, while for PSF films, $W_f$ decreased by 70%. But, does a decrease in $W_f$ mean their toughness has decreased?

5.3.2 Essential Work of Fracture Experiments

Figure 5.3.2.1 (top) shows EWFM results on notched specimens for $w_f$ as a function of ligament length ($\ell$) for both PVdF-HFP and PVdF-HFP/15% CNC nanocomposite films. Note that most EWFM experiments use constant film thickness, but for these films, it was difficult to control thickness. We therefore included results for all thicknesses in the EWFM plots. The variations in thickness may have contributed to scatter in results, but such thickness effects are addressed in more detail below. The slope of EWFM results ($\beta w_p$) decreased from pure PVdF-HFP films to CNC nanocomposite indicating a reduction in plastic ductility. For 15% CNC films, the slope, was close to zero with only a slight increase with increasing ligament length. Extrapolation to zero ligament length gave essential work of fracture for pure films of $w_e = 22.5 \pm 8.3 \text{ kJ/m}^2$. For 15% CNC films, the toughness increased to $w_e = 34.5 \pm 5.2 \text{ kJ/m}^2$ (the uncertainties are ± one standard error
Figure 5.3.1.1: Mechanical testing results from stress-strain curves for nanocomposite films. Top: PVdF-HFP and PVdF-HFP/15% CNC films. Bottom: PSF and PSF/15% CNC films.
for the linear fit). For PSF (Fig. 5.3.2.1 (bottom)), the addition of 15% CNC decreased the slope ($\beta w_p$), which was consistent with observation that CNC made the PSF less deformable. CNC addition changed toughness from $w_e = 13.3 \pm 2.5$ kJ/m$^2$ for pure PSF to $w_e = 10.1 \pm 3.4$ kJ/m$^2$ for PSF/15% CNC, but this change was not significant within one standard error ($\pm 68\%$ confidence).

Contrary to the dramatic drop in $W_f$ for unnotched films, the toughness as measured by $w_e$ increased with CNC addition for PVdF-HFP and caused little or no decrease for PSF. The proponents of EWFM [20, 22] contend that $w_e$ is a better measure of toughness than $W_f$. In our films the drop in $W_f$ was likely caused by loss of ductility rather than inherent toughness. When toughness is separated from ductility, CNC addition increases the toughness of PVdF-HFP films. Even in PSF where no increase was observed, the fact that toughness did not decrease suggests that the CNC addition has enhanced toughness enough to overcome the overall decrease in ductility. If we assume that the polymer structure does not change with CNC addition, the increase in the fracture toughness suggests good interfacial properties and a sufficient filler density to retard crack propagation.

5.3.3 Interface Modeling

One way to validate interface quality, as suggested by enhanced properties above, is to compare the observed increase in modulus to theoretical predictions for a short fiber composite modulus using a model that accounts for interfacial properties. Nairn and Shir Mohammadi [27] recently developed an enhanced shear lag model for short fiber composites that explicitly models imperfect interfaces on both the fiber sides and the fiber ends. It is called the end-capped shear lag model. The interface is modeled using interfacial stiffness terms — $r_f D_n$ and $r_f D_t$ — where $r_f$ is the fiber radius and $D_n$ and $D_t$ are imperfect interface parameters for normal and tangential loading that vary from 0 for a debonded
Figure 5.3.2.1: Work of fracture $w_f$ vs. ligament ($\ell$) plots to find the essential work of fracture ($w_e$). Top. PVdF-HFP ($\circ$) and PVdF-HFP/15% CNC ($Square$). Bottom. PSF ($\circ$) and PSF/15% CNC ($Square$). Dashed lines represent ± one standard error for the linear fit.
interface to $\infty$ for a perfect interface [28]. Although the end-capped model was verified by comparison to numerical models, it has two problems. As introduced, the model only applies for aligned short fiber composites and like all other numerical and analytical models, it degenerates to a lower bound result when the fiber to matrix modulus ratio gets high ($> 100$). The appendix describes the model and extends it to handle both randomly oriented composites and composites with soft matrices. This section applies the extended model to the current experiments.

If all material properties are known except the interfacial properties, modeling calculations can give information about the interface. The CNC fibers used here were estimated to have modulus $E_f = 105$ GPa, Poisson’s ratio $\nu_f = 0.28$, aspect ratio $\rho = 18$, and diameter $r_f = 10$ nm. For PSF, the matrix properties were measured or estimated as modulus $E_m = 1.2$ GPa and Poisson’s ratio $\nu_m = 0.33$. For this material, the fiber to matrix modulus ratio is $R = E_f/E_m = 87.5$. Because $R < 100$, the properties can be calculated using the end-capped shear lag model (see Appendix). If the interfaces are assumed perfect ($r_f D_n = r_f D_t = \infty$) the calculated composite modulus with 15% fibers is 2.9 GPa, which is above the measured result of 1.8 to 2.0 GPa (see Fig. 5.3.1.1). If we assume the difference is caused by imperfect interfaces, the experimental result can be fit by setting $r_f D_n = r_f D_t = 250$ MPa.

For PVdF-HFP, the matrix properties were measured or estimated as modulus $E_m = 0.55$ GPa and Poisson’s ratio $\nu_m = 0.33$. For this material, the fiber to matrix modulus ratio is $R = E_f/E_m = 190$. Because $R > 100$, the properties can be calculated using shear lag model calibrated for soft matrices that add 93% of the end-capped model with 7% of a fiber effectiveness method (see Appendix). In this model the PVdF-HFP composite with 15% CNC and perfect interfaces is predicted to have modulus of 2.3 GPa. The experimental results can be fit by adjusting the interface parameters to $r_f D_n = r_f D_t = 350$ MPa.

These calculations show the interface properties for PSF and PVdF-HFP are simi-
lar with PVdF-HFP perhaps having a slightly better interface. Because these interface parameters are difficult to measure, there are few results to help decide what values constitute a “good” interface. Some previous results for carbon/epoxy used Raman methods to directly observe stress transfer into the fiber and the results could be fit to determine interface parameters [29]. The result for sized carbon fibers with a known good interface had $r_f D_t = 300$ MPa. By analogy, the CNC composite here can be characterized as having good interfaces. More details about fitting nanocomposite experiments with interface properties will be reported in a future publication [30].

5.3.4 Fractography

Although fillers can reduce ductility (as observed by slope of EWFM experiments), when viewed as energy per increment of crack growth, fillers can block crack propagation and increase toughness (as shown schematically in Fig. 5.3.4.1). For this mechanism to be effective, there needs to be a good interfacial bond between matrix and fibers and enough fibers to inhibit crack growth. A weak interface causes fiber pull-out and is less effective at inhibiting crack propagation. Too few fibers decreases the probability of blocking the crack.

To look for evidence of these mechanisms in our composites, we used fractography
of the fracture surfaces for pure polymer and for CNC composites. Figure 5.3.4.2 shows scanning electron microscopy (SEM) images of the fracture surface for both pure PVdF-HFP and PVdF-HFP/15% CNC. In pure PVdF-HFP the crack surface is smooth with straight propagation. In contrast, with 15% CNC the crack was not straight and the surface was rough, presumably because propagation was deflected by the CNCs. In other words, CNC addition to the polymer gave a local increase in the fracture energy as the crack propagated more through the weaker areas and thus deviated from straight crack propagation. Such a crack path may explain the observed increase in essential work of fracture. Lin et al. [31] showed similar crack deviation behavior in polypropylene filled with 20% CaCO₃ nanoparticles and saw an increase in fracture toughness (as measured by impact tests).

SEM images of fracture surfaces for pure PSF and PSF/15% CNC films show some similarities and some differences (Fig. 5.3.4.3). In pure PSF, like pure PVdF-HFP, the crack propagation is clear and straight. The addition of 15% CNC (Fig. 5.3.4.3 right) shows deviation from a straight crack. Like PVdF-HFP, the crack in filled PSF is scattered on the fracture surface, but unlike PVdF-HFP, the fibrous structure of the fracture surface of PSF/15% CNC suggests that some CNC fibers have pulled-out during crack propagation.
propagation. Greater fiber pull out for PSF is consistent with a slightly poorer interface in PSF/CNC compared to PVdF-HFP/CNC (based on interface modeling) and slightly reduced essential work of fracture. We could not confirm the existence of CNC pull-out on the fracture surface due to the experimental difficulty of beam sensitivity in the SEM, which prevented sufficiently high magnification to allow direct observation of CNCs.

We conclude that CNC addition to both polymers scattered crack propagation from a straight line which tended to maintain high crack propagation toughness despite loss of ductility. Comparing the two nanocomposites suggested two reasons toughness enhancement was greater for PVdF-HFP than for PSF nanocomposites. First, modeling suggested the interface in PVdF-HFP/CNC is better than for PSF/CNC, which is consistent with SEM suggesting more fiber pull out for PSF. Second, because PVdF-HFP density of almost 50% higher than PSF, the PVdF-HFP/CNC composite with 15% fibers by weight had more fibers than the comparable PSF/CNC composite. If fibers with a good interface are diverting cracks, then the PVdF-HFP/CNC composites will have more crack-diverting fibers and therefore greater potential for enhanced toughness.
5.3.5 Specimen Thickness Effects

Because it was difficult to control thickness in specimens prepared using solution casting, our specimen thicknesses ranged from 20 to 80 µm. This variation raises a concern about the best way to measure \( w_e \), but also provides an opportunity to probe thickness dependence of that property. The EWFM for plane stress toughness limits specimen ligament lengths to the range \( 3t < \ell < W/3 \). The high end is to minimize edge effects and keep plastic work confined to the ligament area. The lower end is used to keep the specimens in a state of pure plane stress. Experiments show that within this range, the net stress in the ligament at peak load is constant and close to the plane stress yield strength of a double edge notched specimen [24]. In contrast, for \( \ell < 3t \), the net stress increases indicating a mixed plane stress/plane strain stress state. Saleemi and Nairn [24] further suggested that extrapolating experiments for \( \ell < 3t \) to zero ligament length can determine a plane strain essential work of fracture. But the experiments here avoided that region and instead maintained all specimens within the \( 3t < \ell < W/3 \) range. Although this approach assures a plane stress \( w_e \), thickness dependence in \( w_e \) could obscure the results or contribute to scatter.

Despite the frequent theoretical prediction that \( w_e \) should increase with thickness [20], few experiments have been conducted. Priest and Holmes [32] studied thickness effects in steels and saw only small effects. Levita et al. [33] examined rigid PVC and saw \( w_e \) increase with thickness. To investigate the thickness effect in thin CNC films, we reanalyzed all experiments by fitting to a 3D surface representing the fracture energy as a function of both ligament length (\( \ell \)) and thickness (\( t \)). Both theory and experiments suggest that fracture energy is linear in \( \ell \) for constant \( t \), but has unknown (and possibly nonlinear) dependence on \( t \) (for constant \( \ell \)). In brief, we refit results using a 3D fracture
energy equation of:

\[ w_f(\ell, t) = w_e(t) + \beta w_p \ell \]  

(5.3.1)

where unknowns \( \beta w_p \) and the thickness dependence of \( w_e(t) \) were determined by fitting a semi-parametric regression surface to the data. This surface was linear in the \( \ell \) dimension and had a penalized smoothing spline to fit the non-linearity in the thickness dimension. The fitting was done with R using a generalized additive model function (the \texttt{gam()} function from the \texttt{mgcv} package [34, 35]). This function \texttt{gam()} automatically estimates the trade-off between reducing the non-linearity of the splines and fitting the data using generalized cross-validation. Although it would be preferable to allow thickness dependence in \( \beta w_p \) as well, we did not have enough experiments to resolve that much detail and therefore choose to focus on thickness dependence of \( w_e(t) \). Furthermore experimental observations have suggested that \( \beta w_p \) is less affected by ligament stress state [24] and by thickness [33].

The fracture energy surface fits for PSF and a PSF/15% CNC are given in Fig. 5.3.5.1. The dots show all experimental points. Cross sections of these plots at constant thickness show the assumed linear dependence of \( w_f(\ell, t) \), but the intercepts of those lines may depend on thickness. The essential work of fracture as a function of thickness is given by the front surface of these plots (a cross section at \( \ell = 0 \)). Figure 5.3.5.2 plots these \( \ell = 0 \) contours together with error estimates (± one standard error for the fit) for PSF and a PSF/15% CNC and for PVdF-HFP and PVdF-HFP/15% CNC. Comparing the unreinforced polymers, \( w_e \) for PSF is relatively constant, but appears to reach a peak toughness for \( t = 45 \mu m \) and then decreased for thinner films. In contrast PVdF-HFP toughness increases as thickness decreases. Comparing CNC reinforced polymers to the unreinforced polymers, the \( w_e \) is always equal to or greater in the composites. This result reinforces conclusions above that adding CNC enhances toughness when measured using
Figure 5.3.5.1: 3D plot for the work of fracture ($w_f$) as a function of ligament ($\ell$) and thickness in PSF (top) and for PSF/15% CNC (bottom).
crack propagation methods such as the EWFM. The two composites, however, differ in thickness dependence. The toughness of PSF/15% CNC composites increased for thinner files while it decreased for PVdF-HFP/15% CNC.

With the exception of the PVdF-HFP/15% CNC results, all $w_e$ for our thin films tended to increase as thickness decreased. This result is contrary to theoretical predictions \cite{20} and prior experiments \cite{33}. But the theoretical predictions are based on simplified crack opening displacement arguments that would not account for other material issues affecting fracture and the prior experiments were on much thicker films. For example, the toughness of thin titanium sheets was observed to increase or decrease with thickness depending on crack direction and on texture of the material \cite{36}. Although CNC nanocomposites are not the same as titanium, our experiments suggest that alternative effects of thickness, such as texture, are more important than prior analyses based only on crack opening displacement effects.
5.3.6 Fracture Properties

We can calculate toughness as a stress intensity factor ($K_c$) for our films using Eq. 5.1.2 for plane stress conditions where $G_c$ is set equal to measured $w_e$. Although this calculation could be done for each film, we undertook a Monte Carlo simulation to get information about toughness and variability in toughness. In brief, we generated specimens with a range of thicknesses matching our experimental thicknesses. For each specimen the modulus was assigned randomly using the mean and standard deviation for each film and $G_c$ was assigned randomly using the uncertainty range as a function of thickness from Fig. 5.3.5.2. Finally, $K_c$ was calculated by Eq. 5.1.2 (plane stress conditions). The variability of these results values were used to estimate uncertainty in toughness.

Figure 5.3.6.1 shows the plane stress $K_c$ results for all films. The stress intensity factor, $K_c$, shows that the addition of 15% CNC in PVdF-HFP increased the toughness by $\sim 100\%$ and for PSF the toughness increased by about 16%. These results are consistent with all previous results. The reason $K_c$ for PSF increased slightly while $w_e$ decreased is because the $K_c$ calculations better accounted for thickness effects while the $w_e$ analysis ignored thickness effects. By both methods the toughness of PSF/15% CNC retained the toughness of pure PSF ($i.e.$, no significant degradation in toughness).

5.4 Conclusion

In the studied systems, CNC addition decreased ductility, but increased the toughness, as measured by the EWFM, or had no detrimental effect on toughness. Modeling and fractography suggested that the mechanisms for increased or retained toughness are a good fiber/matrix interface and crack scattering around fibers during crack propagation. Toughness values for these thin films depended on thickness, although the thickness variation
differed from prior concepts developed for EWFM experiments.

These conclusions about toughness differ from some prior nanocomposite studies that relied on total work of fracture experiments rather than fracture mechanics methods. We showed that our films also decreased in total work of fracture, but using that property to characterize toughness may be misleading. Our claim is that EWFM experiments provide a better evaluation of material toughness.

5.5 Appendix

Mean-field modeling for composite properties with randomly oriented or partially aligned fibers has two steps. The first step is to find properties of a unit cell containing aligned fibers [27, 28]. The second step is to use mean-field averaging to find properties of randomly oriented composites.

The first step will result in $E_A$, $E_T$, $\nu_A$, $\nu_T$, and $G_A$ for the five independent mechanical properties of the transversely isotropic, aligned-fibers, unit cell (axial and transverse
tensile moduli and Poisson ratios and axial shear modulus, respectively). $E_A$ can be found using the recent end-capped shear lag model [27]. This model applied optimal shear lag methods [37, 38, 39] to an axisymmetric unit cell where a cylindrical fiber with radius $r_f$ and length $l_f$ is encased in a cylinder of matrix with radius $r_m = r_f + \Delta$ and length $l_m = l_f + 2\Delta$. In other words, the distance from the fiber side to the unit cell side ($\Delta$) is set equal to the distance from the fiber end to the ends of the unit cell. All fiber matrix interfaces were modeled using imperfect interface parameters $r_f D_n$ and $r_f D_t$ where $D_n$ and $D_t$ are interface stiffnesses for normal and tangential sliding (when $D = 0$, the interface is debonded, $D = \infty$ is perfect interface, and all other values are imperfect [28]).

The axial modulus from the end-capped model, $E_{EC}$ was derived to be [27]:

$$\frac{E_2}{E_{EC}} = 1 + \left( \frac{E_f}{E_m} - 1 \right) (V_1 - V_f) + \frac{E_f V_f}{E_m V_m} \Lambda(\rho) \quad (5.5.1)$$

where $E_i$ is modulus and $V_i$ is volume fraction. Subscripts $f$ and $m$ refer to fiber and matrix, but $V_1 = r_f^2 / r_m^2$ is fiber volume fraction ignoring the end caps and $E_2 = E_f V_1 + E_m (1 - V_1)$. The key function of aspect ratio ($\rho$) was derived to be:

$$\Lambda(\rho) = \frac{V_m}{V_2} \left( 1 + \frac{E_2}{E_f} \frac{\tanh(\beta_1^* \rho)}{\beta_1 \eta} + \frac{E_2}{\eta E_f} \frac{\tanh(\beta_2 \rho)}{\beta_2} \right) \quad (5.5.2)$$

where $\beta_1^* = (V_1 - V_f) \beta_1 / (2V_f)$, $\eta = E_m V_2 / (r_f D_n)$,

$$\Lambda_1(\rho) = \left( 1 + \left( 1 - \frac{E_2}{E_f} \right)^2 \frac{\tanh(\beta_1^* \rho)}{\beta_1 \eta} \right) \frac{\tanh(\beta_2 \rho)}{\beta_2 \rho} \quad (5.5.3)$$

$$\beta_1^2 = -\frac{4G_m V_2}{E_m (V_2 + \ln V_1)} \quad (5.5.4)$$

$$\beta_2^2 = \frac{4E_2}{E_f E_m} \frac{V_2}{2G_f} - \frac{1}{G_m} \left( \frac{V_2}{2} + 1 + \ln \frac{V_1}{V_2} \right) + \frac{2V_2}{r_f D_t} \quad (5.5.5)$$
Although numerical calculations \cite{27} show that the end capped shear lag model is very accurate when the fiber to matrix modulus ratio, $R = E_f/E_m$, is less than 100, those calculations also show the model becomes a lower-bound for large $R$. This inaccuracy is not caused by shear lag methods, because all other models, including finite element models, also degenerate to lower bound results for soft matrices \cite{27}. Because our CNCs with PVdF-HFP had $R = 190$, we introduce a correction term to model composites with soft matrices. When $R > 100$, we propose the axial modulus to be

$$E^* = \phi_L E_{EC} + (1 - \phi_L) E_{UB} \quad (0 < \phi_L < 1) \quad (5.5.6)$$

where

$$E_{UB} = \eta_f E_f V_f + E_m V_m \quad (5.5.7)$$

Here $E_{UB}$ is an “upper bound” modulus derived using fiber effectiveness methods advocated in several text books \cite{40}, where $\eta_f$ is found by comparing average stress in a short fiber to the average stress that fiber would have in a continuous fiber composite:

$$\eta_f = \frac{1}{l_f \sigma_\infty} \int_{-l_f/2}^{l_f/2} \sigma_f(x) \, dx \quad (5.5.8)$$

where $l_f$ is fiber length, $\sigma_\infty$ is stress the fiber would have for infinitely long fibers, and $\sigma_f(x)$ is average stress in the fiber cross section at position $x$. Evaluating this integral using the end-capped shear lag stress with imperfect interfaces (rather than the simplistic shear lag used in textbooks \cite{40}) gives

$$\eta_f = 1 - \frac{1 + \left(1 - \frac{E_2}{E_f}\right) \frac{\tanh(\beta_1 \rho)}{\beta_1 \eta} + \frac{E_2}{\eta E_f} \frac{\tanh(\beta_2 \rho)}{\beta_2 \rho}}{1 + \frac{\tanh(\beta_1 \rho)}{\beta_1 \eta} + \frac{E_2}{\eta E_f} \frac{\tanh(\beta_2 \rho)}{\beta_2 \rho}} \quad (5.5.9)$$

For PSF/CNC nanocomposites ($R < 100$), the end-capped shear lag model can be
used directly. For PVdF-HFP/CNC nanocomposites ($R \geq 190$), the model including both $E_{EC}$ and $E_{UB}$ was needed. The only remaining issue is to choose $\phi_L$. We choose $\phi_L = 0.93$ based on comparing Eq. (7.2.1) to numerical results in Nairn and Shir Mohammadi [27]. This value of $\phi_L = 0.93$ appears to fit a wide range of nanocomposites when the matrix is much more compliant than the fibers.

The end-capped shear lag model gives $E_A$ as a function of aspect ratio and interface, but mean-field modeling needs $E_T$, $\nu_A$, $\nu_T$, and $G_A$ as well. Fortunately, both numerical [27] and analytical [41] modeling shows that all other properties are only weakly dependent on aspect ratio. Assuming they are independent of aspect ratio, they can be found for any aspect ratio, such as for continuous fiber composites. All remaining unit cell properties therefore used the Hashin’s analysis [28] for properties of a continuous fiber composite including effects of imperfect interfaces.

The final step is to use mean field methods for averaging unit cell properties. Here we assumed the nanocomposite films are statistically isotropic in the plane of the film (i.e., fibers tend to lie in the plane of the film). For this special case, an upper bound modulus can be found from unit cell properties using [1]:

$$E_c \leq 4U_2 \left(1 - \frac{U_2}{U_1}\right)$$  \hspace{1cm} (5.5.10)

$$U_1 = \frac{E_A(3 + 2\nu'_A) + 3E_T + 4G_A(1 - \nu_A\nu'_A)}{8(1 - \nu_A\nu'_A)}$$  \hspace{1cm} (5.5.11)

$$U_2 = \frac{E_A(1 - 2\nu'_A) + E_T + 4G_A(1 - \nu_A\nu'_A)}{8(1 - \nu_A\nu'_A)}$$  \hspace{1cm} (5.5.12)

where $\nu'_A = \nu_A E_T / E_A$ and $\nu_T$ is not needed.

Bibliography


An experiment is a question which science poses to Nature, and a measurement is the recording of Nature’s answer.

Max Planck

Voice of Trees: Fabrication of Flexible Self-Aligned Nanocomposite Sensors

The content and orientation of nanoparticles in polymer matrix has significant effect on properties of nanoparticles, and these properties can also be to design tailored nanocomposites with unique mechanical, electrical, thermal and optical properties. However, using high content nanoparticles or aligned nanoparticles in composites faces variety of challenges due to high tendency of nanoparticles to agglomeration, difficulty of achieving uniform dispersion, and last but not the least the cost of nanoparticles. Here, we report
a fabrication process of multi-functional nanocomposite film sensors with various content of aligned cellulose nanocrystals (CNC), as an inexpensive renewable nanomaterial. CNC is a stiff nanomaterial that has shown piezoelectric properties and can have different surface modification. With using this approach, we could reach up to 47% aligned CNC content embedded in the polymer matrix without any sign of agglomeration and fabricate tailored nanocomposites with unique mechanical and piezoelectric properties. The fabricated nanocomposites, PVdF/CNC, can be used as tunable smart material.

6.1 Introduction

In a simple word, smart material is a material that has a reversible response to an external change (driving force) [1]. For instance, piezo or pyroelectric materials respectively generate electric current in response to external force or temperature (or radiation) changes and they can be used as a sensor [1]. Most of piezo or pyroelectric materials are ceramics but for some applications flexible sensors are needed [2, 3]. Poly (vinylidene fluoride) (PVdF), and its copolymers are the only commercially available polymer with piezo, pyro and ferroelectric properties [2]. Unlike ceramic piezoelectrics, PVdF has wide frequency range (1mHz to 1GHz), high dielectric strength, low acoustic impedance [2, 3] and can be fabricated in irregular shapes [4, 5, 6]. PVdF has five different crystal structures (α, β, γ, ε and δ) depending on its chain conformation [7, 8, 9, 10]. β phase is desirable for its piezoelectric properties. β phase can be made using two general methods: multi-stage and solution casting [2, 10]. The problem with multi-stage fabrication methods is that they all include the mechanical drawing of PVdF, which is not applicable for microfabrication and irregular shapes [5, 11, 12]. On the other hand, solution-cast PVdF films usually have a high porosity, they are fragile [13, 14] and films have inconsistent thickness [15, 16].
Besides sensors, PVdF can be used for biomedical applications due to its biocompatibility. Some literature suggested PVdF can be used for surgical mesh, suture, cardiovascular and as a support (scaffold) for tissue regeneration (cell growth). The reasons for using PVdF over other polymers for these applications, besides its compatibility, are low in vivo degradation rate, the cell attachment and desirable mechanical properties (e.g. stiffness, strength, and toughness)\[17\] \[18\] \[19\]. For these applications having higher mechanical properties per density would be more desirable \[19\]. In the other word, handling applied load in the body with less weight is superior for biomedical applications. Furthermore, different literature showed \(\beta\) phase PVdF has better cell attachment compare with other crystal structure \[20\], \[21\].

Some research suggested using different nanoparticles to tune the mechanical or microstructural properties of PVdF \[10\], \[13\], \[22\] \[23\] \[24\] \[25\]. For instance, the addition of electrostatically charged nanoparticle increases \(\beta\) phase formation \[13\] without considering about mechanical properties (some of these particles even decreased the mechanical properties of PVdF due to incompatibility) \[26\]. Moreover, most these nanoparticles are toxic and could not be used for biomedical applications.

Here we propose fabrication of a novel nanocomposite using cellulose nanocrystals (CNCs) incorporated into PVdF to enhance \(\beta\) phase PVdF with the possibility to control the stiffness and microstructure of composites depending upon the volume ratio of composite components. CNCs are renewable nanomaterials and have considerably high stiffness. They have been used to fabricate nanocomposites with tunable properties for different applications \[27\], \[28\]. They are extracted from different sources including wood pulp, cotton, bacterizes and tunicates. Wood pulp CNCs are the least expensive one, and they are the most abundant nanoparticle on the planet. The surface of CNC obtains electrostatic charge when is extracted using controlled acid hydrolysis as it was explained
elsewhere [27]. The surface charge depends on the type of the acid used for hydrolysis. Cellulose by itself also can act as a piezoelectric material due to its crystal structure [1][29]. Here, the new single stage solution-casting technique is for fabrication preferentially aligned PVdF/CNCs and eliminate the formation of \( \alpha \) phase PVdF.

6.2 Experiments

6.2.1 Materials

PVdF with density of 1.78 gr.cm\(^{-3}\) and molecular weight of 530000 \( D \) was purchased from Scientific polymer products inc. NY, U.S.A. Sulfonate CNC (S-CNC) dispersed in water (11% solid) was purchased from the University of Maine. Dimethylacetamide (DMAc) was used as the organic solvent and it was purchased from Honeywell Burdick & Jackson Co., MI, U.S.A. For carboxylate-CNC (CNC) mild acid hydrolysis was used for extraction of CNC from wood pulp as explained elsewhere [27]. Scanning electron microscopy (SEM) was used to measure aspect ratio of CNCs (\( \rho = \frac{\text{length}(L)}{\text{diameter}(d)} \)) and ... was used to find the electrostatic charge on surface fibers (\( \zeta \) potential). S-CNC fibers had the average aspect ratio of 18 and diameter of 10 nm and the average \( \zeta \) potential was -50 mV. Average aspect ratio of C-CNC fiber was \( \sim 12 \) and the average \( \zeta \) potential was ... mV.

6.2.2 Fabrication process

DMAc was added to a CNC/water solution (to reach 4 weight% CNC in DMAc). A Roto-vapor (Büchi RE111, Switzerland) was used to completely evaporate water from solution (PVdF does not dissolve in water). PVdF was dissolved in DMAc and was mixed with the dispersed CNC in DMAc to reach the desired weight ratio of CNC in the PVdF com-
posite and stirred for 0.5 hr at $85^\circ$ C to yield a uniform solution. The total solution solids were $\sim 5\%$. The solutions were poured into a metal beaker that is attached to a motor. The beaker was partially sealed with a center-holed cap to contain liquid but evaporate the solvent. The beaker rotated at 1800 rpm and films were cast on the wall of the beaker. A heat gun is applied to the exterior of the metal beaker to control the temperature. All films were cast at below $70^\circ$ C. The casting process for each film was 2-10 hrs depending upon the weight of the used solvent (films thickness could be controlled with the amount of used solution). Casted films were removed from the beaker using deionized water. Figure 6.2.2.1 shows the schematic picture of the centrifugal casting process.

Figure 6.2.2.1: Schematic picture of centrifugal casting process. After pouring solution in the beaker centrifugal force moves the solution on the wall (a) shear on the wall is applied to the solution and contractual force keeps the film in uniform thickness while solvent is evaporating (b) and casted films have preferential alignment (c).
6.2.3 Mechanical testing

All samples were cut carefully with 12.7 mm width and the thickness of each sample was measured using optic microscope (Nikon eclipse E400) for stress calculation. Centrifugal casted films were cut in two directions; tangential (TG) and perpendicular (PR) to the rotation directions. In order to have accurate strain measurement, digital image correlation (DIC) method was used as explained elsewhere [ref]. For speckle pattern on films, micro toner (Toner powder Q2612A cartridge was purchased from Hewlett Packard Palo Alto, CA, USA) was sprayed on samples using custom made air deposition apparatus (M.A. Sutton, personal communication) and heated for 5 mins at 103 °C to melt micro toner. All samples were tested at room temperature using Instron 4301 and 220 N load cell capacity. All pictures for DIC were taken using pointgray camera (GS2-GE-50S5M). Young’s modulus was calculated from the linear part of stress-strain curve for each sample. At least 4 samples were used for each film to calculate young’s modulus. Samples for all other tests were cut from undeformed parts of films.

6.2.4 FTIR

Infrared spectra were obtained using a FTIR spectrophotometer (Thermo Scientific Nicole iS50) in the wave number range of 400 to 3000 cm⁻¹. \( \beta \) phase has two corresponding absorption bands at 445, 511, 598,754, 839, 1280 and 1400 cm⁻¹. For \( \gamma \) phase, characteristic bands are 432, 775, 812, 882 and 1234 cm⁻¹. The vibration bands at 532, 612, 763, 796, 854, 870, and 970 cm⁻¹ correspond to \( \alpha \) phase [6, 7, 8, 9, 10, 16, 30].
6.2.5 X-Ray Diffraction (XRD)

Bruker D8 discover was used for wide angle X ray diffraction. $2\theta$ angle of different planes in the composite films (both PVdF and CNC are crystalline) were measured to investigate crystal structure of PVdF. The operating voltage and the used current were 40 kV and 40 mA. The speed of $2\theta$ scan was $2^\circ\text{ min}^{-1}$ and the increment was 0.05. For cellulose crystals $2\theta$ peaks are $\sim$15-17$^\circ$, 20.5$^\circ$, 22.7$^\circ$ and 34.5$^\circ$ attributed to different planes. 22.7$^\circ$ is $2\theta$ in response to (2 0 0) plane and fibers direction is parallel to [2 0 0] direction of Cellulose crystals [27, 31]. Therefore, XRD beams were fixed on $2\theta = 22.7^\circ$ and all films were rotated 180$^\circ$ ($\phi$ scan) to check the alignment of CNCs (the speed was 10$^\circ\text{ min}^{-1}$ and the increment was 1). $\phi$ scan (rotating composite films in plane with fixed $2\theta$) results were used to find possible alignment of CNCs in centrifugal casted films (see Fig. ??). For each film 3 samples were cut from different parts of films and the average intensity is reported.

6.2.6 Piezoelectric response

A test apparatus was built to measure the amplitude of the in plane piezoelectric behavior as a function of voltage and frequency. The polymer films were sputter-coated with gold and clamped between a set of brass rings with 5 cm diameter. This setup is illustrated in Figure [6.2.6.1]. Because of the fixed boundary, the in plane piezoelectric induced deformation causes the film to deflect out of plane. The amplitude of this deflection was measured in the center of the ring using an IR optical proximity sensor.
6.3 Results

6.3.1 Mechanical test

Most of analytical models predicts the stiffness in the composites as a function of volume fraction rather weight fraction. Therefore we plot of stiffness results as function of volume fraction of CNCs. In order to convert weight fraction of CNC ($w_f$) in the films to volume fraction ($V_f$) equation 1 was used.

$$\frac{\rho_m}{\rho_f}w_f(\%) = V_f(\%)$$  \hspace{1cm} (6.3.1)

The density of CNC ($\rho_f$) and PVdF ($\rho_m$) are 1.5 and 1.78 gr.cm$^{-3}$. Figure 6.3.1.1 shows young’s modulus of composite films ($E_c$) vs. CNC content ($V_f$) in both directions of
Figure 6.3.1.1: Young’s modulus (E) vs. volume fraction of S-CNC ($V_f$) fibers in PR (○) and TG (△) directions. Black solid line shows shear-lag-capped (SLC) model with ODF partial alignment results. dotted line is SLC model in TG with randomly oriented fibers and dashed line shows SLC results for fully aligned composite (a). And comparison of C-CNC (□) nanocomposite vs. S-CNC (○) results in PR direction.

casted films. All films showed higher young’s modulus in PR direction than TG. The reason for this difference, in our believe, would be partial alignment of polymer and CNC (in films with CNC). Addition of CNC increased the stiffness of polymers in both directions. The maximum volume fraction of CNC without agglomeration was 47% $V_f$ (20% wt.). In the plot we showed the results for up to 30 $V_f$ CNC and young’s modulus of composite increased to 4.7 ± 0.4 and 3.3 ± 0.25 GPa in PR and TG directions receptively (for pure PVdF was 1.4 ± 0.1 and 0.8 ± 0.1 GPa). For samples higher than 30 $V_f$ % CNC, fibers get highly aligned and small deviation from PR angle during the test makes a huge difference in modulus. For instance, in 47 $V_f$ % films in PR direction the average young’s modulus was 5.8 ± 1.35 GPa some samples showed up to 7.3 GPa modulus. We increased the amount of samples that used for calculating standard deviation twice but it did not decrease the measured standard deviation. This was not a huge issue in TG direction which was perpendicular to fibers direction. The young’s modulus in TG direction for 47 $V_f$% was 3.6 ± 0.8 GPa.
Figure 6.3.2.1: FTIR results for different films shows with addition of CNC $\alpha$ phase peaks disappear and $\beta$ phase increases.

6.3.2 FTIR

Figure 6.3.2.1 shows wave number peaks of centrifugal casts of films, with different wt.% CNC, between 400 to 1000 cm$^{-1}$. Dashed lines indicate representing peaks (511 and 839 cm$^{-1}$) for $\beta$ phase. For all films, $\beta$ phase is dominated crystal structure. Centrifugal-cast PVdF (pure with CNC) shows a small amount of $\alpha$ phase in the film structure (dotted lines shows $\alpha$ phase peaks). Increasing CNC content in the film composites removed the presence of $\alpha$ phase in films. All films had an inevitable amount of $\gamma$ phase that did not change with the presence of CNC (dash-dotted lines shows the 432, 775 and 812 cm$^{-1}$ peaks for $\gamma$ phase).
6.3.3 XRD

To verify alignment of CNCs embedded in PVdF, first we needed to detect the $2\theta$ peak in response to (2 0 0) plane of CNC in our films. Figure 6.3.3.1 shows the $2\theta$ scan of 4 different films (pure PVdF, 10% CNC, 16% CNC and 20% CNC). 10 % CNC film was the first film that we could detect $2\theta = 22.7^\circ$ because of overlapping with PVdF peaks. $\beta$ phase PVdF has an orthorhombic crystal structure and shows one single peak around 20.3$^\circ$ from the superposition of (1,1,0) and (2,0,0) reflections. Crystal structure of $\alpha$ phase is monoclinic and has peaks around 17-18.5$^\circ$, 20$^\circ$ and 25- 30$^\circ$ attributed to different planes [17, 32]. In composite films with less than 16 wt.% CNC, $\beta$ phase peak overlaps with (2 0 0) plane peak, and changes the intensity of 22.7$^\circ$ peak that make the $\phi$ scan results for alignment unreliable. 22.7$^\circ$ peak for 16 wt.% and 20 % CNC films had enough intensity for $\phi$ scan. Figure 6.3.3.1 shows average $\phi$ scan results of 16 and 20 wt.% films. 90$^\circ$ peaks represent PR direction in both films; 0$^\circ$ and 180$^\circ$ are in respond to TG direction. The intensity of peaks around PR direction is twice higher than TG, which shows a preferential alignment of CNC in PR direction.
6.3.4 Piezoelectric response

To reduce calibration, geometry and background light effects, displacement values are given as relative measurements. Figure 6.3.4.1 shows the effect of CNC on amplitude at different frequency. The addition of CNC increases the amplitude (displacement) and shift the maximum amplitude to a lower frequency that we call it the voice of trees.

6.4 Discussion

Composites with high percentage filler content and no agglomeration need to have a preferential alignment \[33, 34\]. In the other word, particles are ordered. As aspect ratio ($\rho$) gets higher, the preferential alignment is necessary at lower filler volume fraction ($V_f$) to not have agglomeration \[35, 36\]. In traditional composites, High $V_f$ composites can be fabricated by fiber layout, for continuous-fiber composites, or extrusion for short-fiber composites \[35\]. In the extrusion process, polymer matrix has to be heated above the melting point, which might cause a change in properties of nanoparticles (e.g., CNC de-
grades at \(> 180^\circ C\) or polymer matrix. So, for those nanocomposites solution-casing is the only fabrication method. Electrospinning is another method for fabrication of high \(V_f\) aligned nanocomposites, which indeed is the extrusion of composite components in solution and fast evaporation of solvent \([11, 37]\). This method is limited only for fabrication of nanocomposites in the form of fiber or porous media \([10, 17, 38, 39]\).

In all of these practical fabrication processes, mechanical shearing is the driving force for the alignment. Here, centrifugal casting is a versatile approach for solution-casting of nanocomposites with preferential fiber alignment. Centrifugal force makes the solution stay in a uniform thickness along the beaker’s wall and the interaction between solution, with gravity and centrifugal force constantly applies shear on nanocomposite during casting (see Fig. 6.2.2.1). This shear causes the preferential alignment along the beaker’s wall (PR direction). Stiffness modulus in PR direction is higher than TG direction is all of these PVdF/CNC nanocomposite films (see Fig. 6.3.1.1) and, the difference in modulus increases more with CNC content (\(\propto V_f\)). This difference has two potential reasons. First is that the polymer modulus, by itself, is different in two directions, and CNC increases the stiffness in both directions. However, since PR, in comparison to TG has higher stiffness, the increase in the stiffness of composites is more drastic in glassy than rubbery polymers if they both have same interface properties \([35]\). In the other word, the degree of alignment is independent of \(V_f\). Second is that with increasing the content of fibers (CNC) do to electrostatic surface charge on the fibers, they obligate each other from having a degree of freedom (repulsive interaction) and the alignment of fibers increases (see Fig. 6.2.2.1). For samples 16 wt. % and 20 wt. % films modulus difference is drastic (More 1 GPa difference). XRD results also show the change in alignment of CNC fibers at higher CNC content.
The orientation of the fibers embedded in the matrix can be described in a probabilistic form using an Oriented Distribution Function (ODF) \[40\]. The ODF is essentially a probability function (PDF), giving a probability of that a single fiber is laying at a given angle. An analytical estimation of the Oriented Distribution Function (ODF) was found by fitting the XRD intensity curve with a Gaussian function using a least squares routine. The Gaussian function was fitted with an intercept to remove the background, (Equation 6.4.1) and was normalized analytically.

\[
f(\chi) = ae^{-(\chi - \mu)^2 / 2\sigma^2} + b
\]  

(6.4.1)

So the ODF becomes

\[
ODF(\chi) = Ce^{-(\chi - \mu)^2 / 2\sigma^2}
\]  

(6.4.2)

Here, \(\chi\) is the angle (from 0 to 180°), \(\mu\) and \(\sigma\) are the mean, and standard deviation of the alignment and \(C\) is the normalizing constant respectively. A \(\mu\) of 90° would indicate that the average alignment of the fibers was in the PR direction. The standard deviation \(\sigma\) indicates the level of alignment of the fibers with each other. As \(\sigma \to 0\) the fibers become perfectly aligned and as \(\sigma \to \infty\), the fibers become uniformly random.

Figure 6.3.3.1 shows the fit of Eq. 6.4.2 to the intensity data (\(\phi\) scan). The \(\mu\) coefficients indicate that the average alignment of the nanocomposite with 20 wt.% fibers was closer to the PR direction, with a difference of by 4.4° as opposed to \(\sim 10.0°\) for the 16 % fiber material. Furthermore, the standard deviations (\(\sigma\)) indicate more level of alignment (the alignment of fibers with each other) with increasing the amount of fiber in the composite (see Table 6.1). For example, the lower value of \(\sigma\) for the 20 wt.% indicates a better alignment of the fibers with each other.

If we plugin ODF results into an analytical short-fiber model, we can predict the
modulus of our partially aligned nanocomposites. Among analytical models Shear-Lag-Capped (SLC) is the only model that counts for imperfect interface [35, 41, 42]. Figure 6.3.1.1 shows both experiment results and SLC prediction in both directions. Unlike TG direction, in PR direction after around 15 $V_f$ % the modulus increases drastically due to preferential alignment of CNCs. Figure 6.4.0.2 compares fracture surface of 5 wt.% and 20 wt.% films in both TG and PR directions. In TG direction, for both films, the shear pattern can be noticed (see Fig. 6.4.0.2 (a) (b)). CNC fiber tips are visible in both direction and PR direction is slightly higher. On the other hand, in 20 wt.% film the difference is drastic due to a higher degree of alignment in PR direction.
Comparing S-CNC and C-CNC results (see Fig. 6.3.1.1 (b)) in PR direction, both experiments and SLC model shows, this self-alignment of fibers is proportional to $\frac{1}{\rho}$. Some literature suggests this drastic increase as percolation effect [28, 43], which in our believe, can be an increase in the alignment of fibers.

This partial alignment is similar to the formation of wood cell-wall where with increasing the $V_f$ of cellulose, the microfibril angle (crystals angle) gets closer to longitudinal direction [44, 45]. In cell-wall, $S_2$ layer has the maximum CNC content ($\sim 60 \text{–} 70\%$) considering amorphous parts of cellulose [27, 46, 47].

For high $V_f$ CNC content ($> 25\%$), the solution was viscous and nanocrystals could not arrange parallel, in PR direction, before solvent evaporation. However, with increasing the amount of solvent (The total solution solids reduced to $\sim 3\%$) we reached up to $47\%$ CNC in films without any sign of agglomeration and the stiffness of nanocomposites
is considerably higher than pure polymer (~400–500% increase). Also, like wood cell-wall, the stiffness is considerably higher in PR (or longitudinal) direction in comparison to TG direction, and this small angle in fiber orientation has an effect of stiffness of TG direction as well. Figure 6.4.0.3 shows the fracture surface of 47 $V_f\%$ and agglomerated 50 $V_f\%$ PVdF/CNC films in PR direction where CNCs are aligned in one, agglomerated and collapsed in the other one.

![Fracture surface comparison](image)

Figure 6.4.0.3: Compare PR fracture surface of 47 $V_f\%$ and 50%. For 47 $V_f\%$ fibers are still in order (a) but in 50 $V_f\%$ fiber agglomeration is obvious and fibers are in different orientations.

During the casting, in pure PVdF films with the absence of CNC, centrifugal force bring solution up to the wall (see Fig 6.2.2.1) and the shear between wall and solution exist during the whole casting process. DMAc is a polar solvent and dipolar interaction of DMAc-PVdF as it was explained elsewhere [7,16] causes the formation of $\beta$ phase with the assistance of shear (see Fig. 6.4.0.4 (a)). FTIR results of pure PVdF shows a small amount of $\alpha$ and $\gamma$ phases. With the addition of electrostatic charged CNC fibers, $\alpha$ phase does not form due to the repulsive interaction between $F^-$ and negatively charged CNC (see Fig. 6.4.0.4 (b)). In the other word, CNC acts ad nucleation agent for $\beta$ and $\gamma$ phase formation. Also, XRD results confirms disappearance of $\alpha$ phase with the addition of CNC (see Fig. 6.3.3.1 (a)). Being able to shift the maximum power at different frequency
can be used for tunable sensors that are more sensitive to specific frequency. Therefore, with controlling the ratio of CNC and PVdF, it is possible to fabricate tunable smart nanocomposites with different mechanical and structural properties.

Also, by increasing the temperature of films (post heat treatment nanocomposite films), we could reach to 135°C without any change in the composite structure (FTIR results were identical in PVdF/CNC films). For higher temperature ( > 135°C) nanocomposites start to turn brown which is an indication of CNC degradation. Figure 6.4.0.5 show pure PVdF and nanocomposite films before and after post treatment at different temperature. Post treatment was done using compression for around an hr at different temperature. visual inspection of post treated films shows more uniform thickness and more transparency. Post treatment was only done to study the structure of PVdF/CNC nanocomposites at higher temperature and films were not used for other studies (e.g. piezo effect, fiber orientations and more).
6.5 Conclusion

Here, we introduced a new fabrication method for solution casting (centrifugal casting) of PVdF/CNC polymer nanocomposites with preferential alignment. With addition of CNC (up to 47%) in PVdF, we significantly increased the elastic modulus of nanocomposite at different directions (more than 400% increase). Also, we used XRD to measure the orientation of CNC nanocrystal embedded in PVdF polymer matrix and used ODF to find the degree of alignment in for different volume fraction ($V_f$) of CNC in PVdF/CNC nanocomposites. Furthermore, to predict the Young’s modulus of fabricated PVdF/CNC nanocomposites, we used SLC model for unit cell properties, and averaged the elastic properties based on ODF results, using mean-field, and our prediction was well-fitted.
with the experiments (young’s modulus of PVdF/CNC nanocomposites).

Incorporation of CNC (with negatively charged surface) with different volume fraction ($V_f$) in PVdF eliminates $\alpha$ phase crystal structure formation in nanocomposites and lead to formation of piezoelectric $\beta$ phase (and $\gamma$ phase). We used FTIR and XRD to study the crystal structure of PVdF/CNC nanocomposites and both results showed addition of CNC only forms $\beta$ phase (using solution casting at $<70^\circ$). Furthermore, our vibration results showed that increasing the amount of added CNC ($V_f$) in PVdF increases the amplitude of vibration (voice of trees) and decreases the frequency of maximum vibration. PVdF/CNC nanocomposites hold the $\beta$ phase structure even by increasing up to melting point of PVdF. Combination PVdF and CNC can be used for fabrication of flexible sensor with different mechanical properties, and electrical properties (with different amplitude and sensitive to different frequencies).

Bibliography


Nobody ever figures out what life is all about, and it doesn’t matter. Explore the world. Nearly everything is really interesting if you go into it deeply enough.

Richard Feynman

Summary and suggestions for future works

In this work we tried to develop a new design model to predict elastic properties (and other mechanical properties) of different nanocomposites (CNC nanocomposites in particular) based on the properties of their components (polymer matrix properties, nanoparticles properties and the interface between particles and matrix). We had five steps to achieve our goal, In the first step we used a new FEA method (Monte Carlo FEA with bounded displacement boundary condition (BVE)) to numerically model the elastic properties of nanocomposites, and explain why traditional methods (FEA modeling methods) underestimate the properties and predict lower properties than experiments. Second, we
introduced a new analytical model (shear-lag-capped (SLC)) to predict elastic properties of variety range of nanocomposites (from rubbery low stiffness to glassy or high stiffness matrices). Third, we compared experimental results of different nanocomposites with SLC model, and other analytical models, to the best of our knowledge, that are been used for nanocomposites. Fourth, we used essential work of fracture (EWFM) method to measure fracture toughness of both rubbery and glassy cellulose nanocomposites (thin films). Fifth, we introduce a new method for fabrication of preferentially aligned PVdF/CNC nanocomposites, as flexible smart material.

7.1 Numerical model

This part provided basic questions whose answers, in our opinion, provide insights for evaluating past and future literature on modeling short fiber composites. The novel results were to develop a method for bounding the mechanical properties and use that approach to study a regime that is not commonly examined (namely large $R$ and large $\rho$). The numerical experiments showed that for $R < 100$, the bounds are rather close and other numerical and analytical models fall within those bounds and therefore must be close to the correct answer. For $R > 100$, however, the numerical bounds diverge and both analytical methods and prior numerical methods based on periodic displacement boundary conditions degenerate to lower bound results. We do not claim the numerical upper bounds are predicting the modulus of real materials — they are upper bound results and because of the crude mesh are not the best upper bounds possible. But, all efforts to seek refined upper bounds suggest that at large $R$ even improved upper bounds are two or more orders of magnitude higher than results found by prior methods. Given that some experimental results on reinforcement of elastomers [1, 2] exceed predictions by analytical or
prior numerical models, but do not exceed upper bound BVE results, the two options are that current modeling methods are inadequate or that we must abandon continuum mechanics. The upper bound results here demonstrate the answer might be the former. Furthermore we showed periodic boundary condition regenerates results close to lower bound for $R > 100$ and underestimate the properties of rubbery short fiber composites.

7.2 Analytical model

Analytical models typically treat a single fiber. The Eshelby/ Mori-Tanaka approach \cite{3, 4} and the new shear lag method presented here, agreed well with lower bound, numerical, single-fiber models, but gave no information about upper bound modulus for high $R$. The new shear lag method adds modeling for imperfect interfaces. It is not worth the effort to seek “improved” analytical models because there is little room to improve agreement with numerical modeling on the same structure. The more interesting problem is how to avoid degenerating to a lower bound results. The next tasks for short fiber composite modeling should be to develop a new approach to analytical modeling that can predict upper bound moduli for all values of $R$ and to extend that modeling to composites with non-aligned fibers by averaging over a fiber distribution function \cite{5}.

Although numerical calculations \cite{6} show that the end capped shear lag model is very accurate when the fiber to matrix modulus ratio, $R = \frac{E_f}{E_m}$, is less than 100, those calculations also show the model becomes a lower-bound for large $R$. This inaccuracy is not caused by shear lag methods, because all other models, including finite element models, also degenerate to lower bound results for soft matrices \cite{6}. Because our CNCs with PVdF-HFP had $R = 190$, we introduce a correction term to model composites with
soft matrices. When \( R > 100 \), we propose the axial modulus to be

\[
E^* = \phi_L E_{EC} + (1 - \phi_L) E_{UB} \quad (0 < \phi_L < 1)
\]

(7.2.1)

where

\[
E_{UB} = \eta_f E_f V_f + E_m V_m
\]

(7.2.2)

Here \( E_{UB} \) is an “upper bound” modulus derived using fiber effectiveness methods advocated in several text books \[7\], where \( \eta_f \) is found by comparing average stress in a short fiber to the average stress that fiber would have in a continuous fiber composite:

\[
\eta_f = \frac{1}{l_f} \int_{-l_f/2}^{l_f/2} \sigma_f(x) \, dx
\]

(7.2.3)

where \( l_f \) is fiber length, \( \sigma_\infty \) is stress the fiber would have for infinitely long fibers, and \( \sigma_f(x) \) is average stress in the fiber cross section at position \( x \). Evaluating this integral using the end-capped shear lag stress with imperfect interfaces (rather than the simplistic shear lag used in textbooks \[7\]) gives

\[
\eta_f = 1 - \frac{1}{1 + \frac{\text{tanh}(\beta_1 \rho)}{\beta_1 \eta} + \frac{\text{tanh}(\beta_2 \rho)}{\beta_2}}
\]

(7.2.4)

For rubbery nanocomposites (\( R > 100 \)), the model including both \( E_{EC} \) and \( E_{UB} \) was needed. The only remaining issue is to choose \( \phi_L \). We choose \( \phi_L = 0.93 \) based on comparing Eq. (7.2.1) to numerical results in Nairn and Shir Mohammadi \[6\]. This value of \( \phi_L = 0.93 \) appears to fit a wide range of nanocomposites when the matrix is much more compliant than the fibers.

The end-capped shear lag model gives \( E_A \) as a function of aspect ratio and interface, but mean-field modeling needs \( E_T, \nu_A, \nu_T, \) and \( G_A \) as well. Fortunately, both numerical
[6] and analytical [5] modeling shows that all other properties are only weakly dependent on aspect ratio. Assuming they are independent of aspect ratio, they can be found for any aspect ratio, such as for continuous fiber composites. All remaining unit cell properties therefore used the Hashin’s analysis [8] for properties of a continuous fiber composite including effects of imperfect interfaces. The final step is to use mean field methods for averaging unit cell properties. Here we assumed the nanocomposite films are statistically isotropic in the plane of the film (i.e., fibers tend to lie in the plane of the film).

Among all models that were discussed (which can be used to predict the stiffness of nanocomposites, the shear-lag-capped (SLC) model with solution map (considering both interface and $\phi_L$) showed better results, for wide range of nanocomposites, than other models. Although, interface properties ($D_t$ and $D_n$) play an important role in the modulus of nanocomposites, experimental measurement of interface properties on the nanoscale is the ”Achilles’ heel” for stiffness prediction of these composites [9]. But, ($D_t$& $D_n$) can be used as a measurement for interface properties, by comparing with experiments (macro scale), and once it is known between each matrix and nanoparticle, it can used to predict modulus of composite for different volume fractions ($V_f$). As $R$ (stiffness mismatch) gets larger in nanocomposites, the stiffness predictions get more complicated and more variables are involved (the interface, $\phi_L$, $V_f$, and the relation between these variables). To have more accurate prediction, the effect of $V_f$ and $\rho$ on $\phi_L$, $D_t$ and $D_n$ needs to be considered, which makes the calculation more complex. So, using $\phi_L$ with a solution map [9], which guarantees that the experiments would not exceed the prediction, and offers a rigorous upper bound that can be used to predict the possibility of achieving desired elastic properties in nanocomposites. Furthermore, the experiments indicated that for rubbery nanocomposites (high $R$ value), the stiffness of nanocomposites gets close to upper bound SLC at higher $V_f$ and $\rho$ if the interface is perfect. But, for imperfect interface the
results are close to lower bound, which shows the importance of the interface in the mechanical properties of nanocomposites. Fiber efficiency is a simple way to predict stiffness of nanocomposites. We showed for rubbery nanocomposites ($R > 10^4$), with randomly oriented fibers, the maximum fiber efficiency ($\eta_{f_{max}}^* = 0.02$) is a good approximation for maximum theoretical stiffness based on continuum mechanics, and $\eta_{f_{max}}^*$ increases up to $\sim 0.3$ for glassy nanocomposite ($R < 100$), with perfect interface. But, usually the achievable $\eta_{f_{max}}^*$, in experiments, is lower because of imperfect interfaces.

In our opinion, using $\eta_{f_{max}}^*$ based on what we explained here is an easy way to compare experiment with theories based on continuum mechanics, and the experiment should not exceed the theoretical predictions, and if experiments exceed those prediction, new perhaps a mechanics would needed for modeling the stiffness of nanocomposites.

7.3 Fracture toughness

CNC addition (to polymer matrix with good compatibility) decreased ductility, but could increase the toughness, as measured by the EWFM, or had no detrimental effect on toughness. Modeling and fractography suggested that the mechanisms for increased or retained toughness are a good fiber/matrix interface and crack scattering around fibers during crack propagation. Toughness values for these thin films depended on thickness, although the thickness variation differed from prior concepts developed for EWFM experiments.

These conclusions about toughness differ from some prior nanocomposite studies that relied on total work of fracture experiments rather than fracture mechanics methods. We showed that our films also decreased in total work of fracture, but using that property to characterize toughness may be misleading. Our claim is that EWFM experiments provide a better evaluation of material toughness.
7.4 Multi-functional CNC nanocomposite

In the last chapter, we introduced a new fabrication method for solution casting (centrifugal casting) of PVdF/CNC polymer nanocomposites with preferential alignment. With addition of CNC (up to 47%) in PVdF, we significantly increased the elastic modulus of nanocomposite at different directions (more than 400% increase). Also, we used XRD to measure the orientation of CNC nanocrystal embedded in PVdF polymer matrix and used ODF to find the degree of alignment in for different volume fraction \( V_f \) of CNC in PVdF/CNC nanocomposites. Furthermore, to predict the young’s modulus of fabricated PVdF/CNC nanocomposites, we used SLC model for unit cell properties, and averaged the elastic property based on ODF results, using mean-field, and our prediction was well-fitted with the experiments (young’s modulus of PVdF/CNC nanocomposites).

Incorporation of CNC (with negatively charged surface) with different volume fraction \( V_f \) in PVdF eliminates \( \alpha \) phase crystal structure formation in nanocomposites and lead to formation of piezoelectric \( \beta \) phase (and \( \gamma \) phase). We used FTIR and XRD to study the crystal structure of PVdF/CNC nanocomposites and both results showed addition of CNC only forms \( \beta \) phase (using solution casting at \(< 70^\circ\)). Furthermore, our vibration results showed that increasing the amount of added CNC \( V_f \) in PVdF increases the amplitude of vibration (voice of trees) and decreases the frequency of maximum vibration. PVdF/CNC nanocomposites hold the \( \beta \) phase structure even by increasing up to melting point of PVdF. Combination PVdF and CNC can be used for fabrication of flexible sensor with different mechanical properties, and electrical properties (with different amplitude and sensitive to different frequencies).
Bibliography


